



**Planning Documents
Project No. 60251**

**Supplemental Work Plan
and QAPP Addendum
Phase II
Remedial Investigation**

Prepared for:

**Steering Committee
ACS Site PRP Group**

Prepared by:

**Warzyn Engineering Inc.
Chicago, Illinois**

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**QAPP ADDENDUM (PHASE II)
QUALITY ASSURANCE PROJECT PLAN
REMEDIAL INVESTIGATION/FEASIBILITY STUDY
AMERICAN CHEMICAL SERVICE SITE
GRIFFITH, INDIANA**

Prepared By:

WARZYN ENGINEERING INC.

**2100 Corporate Drive
Addison, Illinois 60101
(708)691-5000**

APPROVALS:

DATE:

**American Chemical Services Steering Committee
Chairman**

Warzyn Site Project Manager

Warzyn Quality Assurance Officer

U.S. EPA Remedial Project Manager

U.S. EPA Region V Quality Assurance Officer

SECTION 1.0 - INTRODUCTION (page 1 of 38)

This document supplements the Quality Assurance Project Plan (QAPP) for the American Chemical Services Site Remedial Investigation/Feasibility Study (RI/FS) in Griffith, Indiana. The changes in the QAPP are presented as an addendum to the approved QAPP, dated May 1989. Phase II RI activities have been established based on the results documented in the Phase I RI Technical Memoranda.

Reference will be made to the previous QAPP document through citation of page numbers, as applicable. Unless changes are noted in this document, the description of activities in the original QAPP remain as stated.

The overall objective of Phase II investigation is to further determine the nature and extent of potential contamination at the site in order to support the activities of the Feasibility Study (FS). Results of Phase II investigation will build on information collected during Phase I to provide a clearer picture of waste characteristics and potential for groundwater contamination.

SECTION 2.0 - TABLE OF CONTENTS (page 3 of 38)

The Table of Contents is unchanged. Modifications made are referenced to the appropriate locations in the original document.

SECTION 3.0 - PROJECT DESCRIPTION (page 7 of 38)

The site characterization described in Section 3 (page 7 of 38) remains as stated. Proposed Phase II activities are described in detail in the Supplemental Work Plan (SWP). The field and sampling activities for each of the Phase II activities are summarized in Table 1 of this QAPP Addendum.

Many of the activities in the Phase II SWP simply increase or re-allocate previously approved sampling procedures and are not included in this QAPP Addendum. However the following sampling and analysis activities were not included in the original Work Plan and QAPP:

- Field screening of VOC concentrations in groundwater.
- Reduction/Oxidation Potential (Redox) testing of field samples while collecting groundwater samples from monitoring wells.
- Dissolved oxygen (DO) testing of field samples while collecting groundwater samples from monitoring wells.
- Analysis for Total Organic Carbon (TOC) in solid matrix samples.

Data use and the associated data quality objectives for the above four activities have been summarized in Table 2 of this QAPP Addendum.

Specific analytical procedures to be used in above activities are contained in Appendix B of this QAPP Addendum.

A summary of Phase II sample numbers and matrices is given in Table 3. A summary of sample containers, sample volumes, preservatives and shipping methods is given in Table 4. The project schedule for Phase II of the ACS Site RI/FS can be found in Table 5.

SECTION 4.0 - PROJECT ORGANIZATION AND RESPONSIBILITIES (page 17 of 38)

Project Organization and Responsibility remain as stated.

SECTION 5.0 - QUALITY ASSURANCE OBJECTIVES (page 5-1)

The QA objectives remain as stated with the following exceptions:

- The last sentence of the second paragraph should refer to Table 2 of this QAPP Addendum in addition to Table 4 of the original QAPP.
- Subsection 5.1.2 (page 21 of 38) CompuChem is amended to include: Samples collected from private wells will be analyzed for TCL organics using methods described in Appendix B1, which provide lower detection limits than CLP protocols. Larger volumes of sample media and MS/MSD samples will be collected for low-detection-limit analyses (Table 4 of this QAPP Addendum). As described in the method description, these analyses will have a similar level of QC effort as CLP protocols.
- Subsection 5.1.2 (page 22 of 38) is amended to include samples to be analyzed for total organic carbon (TOC). This analysis will follow the protocols described in Appendix B-2, with QC effort.
- Subsection 5.1.3 Field Measurement (page 22-38) is amended to include the following:

Field Survey of Groundwater for VOCs

The level of QC effort for the collection and screening of groundwater samples in the field will consist of initial and continuing calibrations at regular intervals as described with the method in Appendix B-3.

Dissolved Oxygen

The level of QC effort for field measurement of dissolved oxygen (DO) will consist of pre-calibration and calibration checks of 1 per 10 samples as described in Appendix B-4.

Redox Potential

The level of QC effort for field measurement of redox potential (L) will consist of zeroing the instrument and checking operation before use and at regular intervals (1 per 10 samples). See Appendix B-5.

- Subsection 5.2 Accuracy, Precision and Sensitivity of Analysis (page 23 of 38) is amended to include the following:
 - Accuracy, precision and sensitivity of the groundwater field screening method are described with the method reference in Appendix B-3.
 - Accuracy of field measured DO will be judged from agreement of instrument readings with aerated water. Agreement will be within ± 0.5 mg/L. Measurement precision will be estimated by periodically (1 per 10 samples) making duplicate readings of samples.

- Accuracy of field measured Redox potential will be judged from agreement of instrument readings with standard buffer solutions. Agreement with standards will be within ± 10 mV of expected value and field measurements will be made to 1.0 mV. Measurement precision will be estimated by periodically (1 per 10 samples) making duplicate readings of samples. If the unit fails to zero it will be replaced.

SECTION 6.0 - SAMPLING PROCEDURES (page 25 of 38)

Specific Phase II sampling procedures are as documented in the original Sampling Plan. Table 4 of this QAPP addendum summarizes sample containers, preservatives, holding times, packing and transport methods.

Documentation of use of specific procedures outlined in the Sampling Plan will be made by initialed entries in the field log book by the Sampling Team Leader. Further details are in the original Sampling Plan.

SECTION 7.0 - SAMPLE CUSTODY AND DOCUMENTATION (page 26 of 38)

Sample custody and documentation will follow procedures as stated.

**SECTION 8.0 - CALIBRATION PROCEDURES, FREQUENCY AND
PREVENTATIVE MAINTENANCE FOR FIELD INSTRUMENTS**

(Page 29 of 38)

This section remains as stated with the following amendment:

Instruments used for groundwater field screening, DO and Redox potential will be calibrated or will undergo internal systems checks, as appropriate, prior to use following procedures recommended by the manufacturer (Appendices B-3, B-4 and B-5 respectively).

SECTION 9.0 - ANALYTICAL SERVICES (page 30 of 38)

This section is ammended to replace Hazelton with CompuChem and the analytical procedures for the organic analysis of private drinking water samples are provided in Appendix B-1. Samples to be analyzed for TOC will follow procedures outlined in Appendix B-2.

SECTION 10.0 - DATA REDUCTION, VALIDATION AND REPORTING (page 31 of 38)

Procedures for data reduction, validation and reporting remain as stated, with the inclusion of Appendix B-1 through B-5 of this QAPP Addendum.

SECTION 11.0 - INTERNAL QUALITY CONTROL CHECKS (page 32 of 38)

This Section is unchanged.

SECTION 12.0 - PERFORMANCE AND SYSTEM AUDITS (page 33 of 38)

This Section is unchanged.

SECTION 13.0 - PREVENTATIVE MAINTENANCE (page 34 of 38)

Preventative maintenance of field instruments will remain as stated, with the following amendment:

Preventative maintenance of Field GC, DO meter and Eh meter are provided with method references in Appendix B-3 through B-5.

Preventative maintenance of instruments used for TOC determination will follow manufactures recommendations.

SECTION 14.0 - SPECIFIC ROUTINE PROCEDURES USED TO ASSESS DATA
PRECISION, ACCURACY AND COMPLETENESS (page 35 of 38)

This Section is unchanged.

SECTION 15.0 - CORRECTIVE ACTION (page 37 of 38)

This Section is unchanged.

SECTION 16.0 - QUALITY ASSURANCE REPORTS TO MANAGEMENT (page 38 of 38)

This Section is unchanged.

Table 1
Phase II Site Investigation Summary
American Chemical Services CERCLA Site
Griffith, Indiana

<u>Activity</u>	<u>Supplemental Work Plan Reference Letter</u>	<u>Description</u>	<u>Result</u>	<u>Utilization of Data</u>	<u>Anticipated Number of Investigation Samples</u>
Water Level Measurements	A	Collect water levels at piezometers, monitoring wells, and staff gauges	Additional water level data	Assess hydraulic gradients and surface water gravel water interactions	None
Upper Aquifer Field Screening	B	15 groundwater samples analyzed by head space/field GC for estimated concentrations	Estimated concentrations of BETX in groundwater samples from upper aquifer	Aid in identification of horizontal extent of groundwater contamination by VOCs for monitoring well placement	FA 20-30 QC analysis
Monitoring Well Installation Lower Aquifer	B C D	Four monitoring wells screened in lower (Valparaiso) aquifer	Lower aquifer water levels and water samples. Concentration of EPA TCL and TAL parameters	1. Extend site stratigraphy 2. Determine vertical hydraulic gradients 3. Determine horizontal hydraulic gradient	LA: 6 Geotech Samples LA: 4 Analytical Samples IS: Water levels
Upper Aquifer	B	Four to eight additional upper aquifer wells installed	Delineate the horizontal and vertical extent of upper aquifer contamination	1. Document water quality in lower aquifer 2. Concentration of EPA TCL and TAL parameters	LA: 4-8 Analytical Samples
Aquifer Matrix Sampling	B	Collect 5 aquifer matrix samples from interior of groundwater plume	Concentration of EPA TCL and TAL parameters	1. Further examine upper aquifer contamination 2. Data for treatability studies	LA: 5 Analytical samples
Private Well Sampling	B	Collect water samples from 1 upgradient and 9 downgradient water supply wells	Concentration of EPA TCL and TAL parameters	Examine for potential contamination surrounding the site	LA: 10 Analytical samples
Aquifer Tests	C	Permeability testing at 4 upper aquifer and 4 lower aquifer locations	Estimates of aquifer permeability	1. Input to contaminant transport model 2. Data to calculate fate and transport 3. Data to evaluate remedial alternatives	None
Sediment Sampling	E	Collect 5 sediment samples from drainageways surrounding site	Concentration of EPA TCL and TAL parameters	Determine if eroding sediments are a potential contamination risk	LA: 5 Analytical

Table 1
(continued)

Phase II Site Investigation Summary
American Chemical Services CERCLA Site
Griffith, Indiana

<u>Activity</u>	<u>Reference Letter</u>	<u>Description</u>	<u>Result</u>	<u>Utilization of Data</u>	<u>Anticipated Number of Investigation Samples</u>
Sediment Sampling	E	Collect 5 near surface soil/ sediment samples	Analyze grain size, and total organic carbon	Determine sorptive properties and natural attenuation capabilities of wetland	LA: 5 Geotechnical samples
Aerial Photograph	F	Infrared color aerial photo taken of site	Infrared color photo	Wetland delineation	None
Field Parameter Analysis	G	During groundwater sample collection, made field measurements including temperature, pH, dissolved oxygen and redox potential	Field parameter of monitoring well water	Aid in assessing treatability of groundwater	IS: 18
Waste Sampling	H	Collect 20 additional waste/soil samples	Physical and chemical extent of buried waste	Data for compatibility and treatability evaluator	LA: 20

Notes:

IS = Insitu Analysis
LA = Laboratory Analysis
FA = Field Analysis

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Table 2

**Summary of Additional or Modified Data Generating Activities
And Associated Data Quality Objectives
American Chemical Services Site**

<u>Activity</u>	<u>Supplemental Work Plan Reference Letter</u>	<u>Use of Data</u>	<u>Data Quality Objectives</u>
Private Well Sampling	B	Examine potential contamination of private water supply wells surrounding the site.	Identify compounds present. Meet performance criteria for TCL organics as stated in CLP SOW 7/87 (or most recent). Meet performance criteria for inorganics and indicators as specified in Appendix F. of original QAPP and Appendix C of QAPP Addendum.
Upper Aquifer Field Screening	B	Aid in identification of horizontal extent of ground-water contamination by VOCs for monitoring well placement.	Estimate concentrations (;50%) of BETX compounds as indicators of VOC contamination. Meet performance criteria specified in Appendix B-3 of QAPP Addendum.
Field Parameter Analysis (D.O. and Redox)	G	Aid in assessing treatability	Meet instrument performance criteria specified in Appendix B-4 and B-5.
Sediment Sampling	E	Determine sorptive properties and natural attenuation capabilities of wetlands.	Meet performance criteria for grain size specified in Appendix F of original QAPP and criteria for TOC specified in Appendix B-2 of QAPP Addendum.

TABLE 3

SUMMARY OF PHASE II SITE CHARACTERIZATION
QAPP ADDENDUM, PHASE II RI
ACS SITE, GRIFFITH, INDIANA

<u>Sample(1)(7)</u> <u>Matrix</u>	<u>Laboratory</u>	<u>Laboratory</u> <u>Parameters(2,5,6)</u>	<u>Study(3)</u> <u>Phase</u>	<u>No. of</u> <u>Investigative</u> <u>Samples</u>	<u>No. of Field</u> <u>Duplicates</u>	<u>No. of</u> <u>Field Blanks</u>	<u>Matrix Spike/(4)</u> <u>Matrix Spike</u> <u>Duplicate</u>	<u>Total No. of</u> <u>Samples</u>
Phase I Monitoring Wells Round 2	Compuchem	TCL Volatiles	2B	6	1	1	1	9
Groundwater	Compuchem	TCL Semi-Volatiles	2B	6	1	1	1	9
	Compuchem	TCL Volatiles	2A 2B	12 *	2	2	2	18 *
	Compuchem	TCL Semi-Volatiles	2A 2B	12 *	2	2	2	18 *
	Compuchem	TCL PCB/Pesticides	2A 2B	12 *	2	2	2	18 *
	Warzyn	TCL Metals (Dissolved)	2A 2B	12 *	2	2	0	16 *
	Warzyn	TCL Metals (Total)	2A 2B	5 *	1	1	0	7 *
	Warzyn	Cyanide	2A 2B	12 *	2	2	0	16 *
	Warzyn	Chloride, Alkalinity, Sulfate	2A 2B	12 *	2	2	0	16 *
	Warzyn	Ammonia, Nitrate-Nitrite, TOC, COD	2A 2B	12 *	2	2	0	16 *
	Warzyn	Total Dissolved Solids	2A 2B	12 *	2	2	0	16 *
	Warzyn	Total Suspended Solids	2A 2B	5 *	1	1	0	7 *
Private Wells (Low Detection Limits)	Compuchem	TCL Volatiles	2	10	1	1	1	13
	Compuchem	TCL Semi-Volatiles	2	10	1	1	1	13
	Compuchem	TCL PCB/Pesticides	2	10	1	1	1	13
	Warzyn	TCL Metals (Total)	2	10	1	1	0	12
	Warzyn	Cyanide (Unfiltered)	2	10	1	1	0	12
	Warzyn	Chloride, Alkalinity, Sulfate	2	10	1	1	0	12
	Warzyn	Ammonia, Nitrate-Nitrite, COD	2	10	1	1	0	12

TABLE 3 (Continued)

Sample(1) Matrix	Laboratory	Laboratory Parameters(2, 5, 6)	Study(3) Phase	No. of Investigative Samples	No. of Field Duplicates	No. of Field Blanks	Matrix Spike/(4) Matrix Spike Duplicate	Total No. of Samples
Sediment	Compuchem	TCL Volatiles	2	5	1	1	1	8
	Compuchem	TCL Semi-Volatiles	2	5	1	1	1	8
	Compuchem	TCL PCB/Pesticides	2	5	1	1	0	7
	Warzyn	TCL Metals	2	5	1	1	0	7
	Warzyn	Cyanide	2	5	1	1	0	7
Natural Soils -Waste Borings	Compuchem	TCL Volatiles#	2	20	2	0	1	23
	Compuchem	TCL Semi-Volatiles#	2	20	2	0	1	23
	Compuchem	TCL PCB/Pesticides#	2	20	2	0	1	23
	Warzyn	TCL Metals#	2	20	2	0	0	22
	Warzyn	Cyanide#	2	20	2	0	0	22
	Warzyn	Volatile Residue#	2	20	2	0	0	22
Aquifer Materials Samples	Compuchem	TCL Volatiles	2	5	1	0	1	7
	Compuchem	TCL Semi-Volatiles	2	5	1	0	1	7
	Compuchem	TCL PCB/Pesticides	2	5	1	0	1	7
	Warzyn	TCL Metals	2	5	1	0	0	6
	Warzyn	Cyanide	2	5	1	0	0	6
Geotechnical Samples- Wells and Sediment	Warzyn	Atterberg limits	2	12	0	0	0	12
	Warzyn	Particle Size	2	12	0	0	0	12
	Warzyn	Total Organic Carbon	2	12	2	0	0	14
	Warzyn	Cation Exchange Capacity	2	8	0	0	0	8
	Warzyn	Total Porosity	2	12	0	0	0	12

Notes

- 1 Samples will be considered low or medium concentration.
- 2 See Appendix B for TCL analyte lists, also up to 30 tentatively identified compounds.
- 3 The star (*) indicates that the number of samples and specific parameters will be determined from Phase 1 and 2A results. Preliminary assessment indicates that up to 9 wells will be sampled for the complete TCL, and the remaining number will be sampled for a reduced parameter list. Also note that Phase 2A sample number is given as the expected maximum.
- 4 Sample numbers do not reflect the additional volume of samples required for matrix spikes and matrix spike duplicate analysis.
- 5 Temperature, pH and specific conductance measurements will be taken in the field for aqueous samples. Qualitative screening with the HNu or OVA will be performed on solid samples.
- 6 The # indicates need for each specific analysis will be determined in field.
- 7 Trip blanks will be included for VOA analysis with each cooler shipped containing liquid samples for VOA analysis.

TABLE 4
SAMPLE QUANTITIES, BOTTLES, PRESERVATIVES AND PACKAGING
FOR WATER, SEDIMENT AND LEACHATE SAMPLES

<u>Analysis</u>	<u>Bottles and Jars</u>	<u>Preservation</u>	<u>Holding Time</u>	<u>Volume of Sample</u>	<u>Shipping</u>	<u>Normal Packaging</u>
WATER AND LEACHATE						
<u>Low Concentration (Organics)</u>						
Semi-Volatiles	Two (four for private wells) 1-liter amber bottle (teflon-lined cap)	Iced to 4°C	5 days until extraction, 40 days after extraction	Fill bottle to neck	Shipped Daily by Overnight Carrier	No. 1 foam liner or vermiculite
Pesticides/PCBs	Two (four for private wells) 1-liter amber bottle (teflon-lined caps)	Iced to 4°C	5 days until extraction, 40 days after extraction	Fill bottle to neck	Shipped Daily by Overnight Carrier	No. 1 foam liner or vermiculite
Volatiles	Two (three for private wells) 40-ml volatile organic analysis (VOA vials)	Iced to 4°C HCL to pH <2	7 days (48 hours for surface water)	Fill completely no headspace	Shipped Daily by Overnight Carrier	No.1 foam liner or vermiculite
<u>Low Concentration (Inorganics)</u>						
Metals (groundwater)	One 1-liter high density polyethylene bottle	Filter through 0.45 μ m filter, HNO ₃ to pH <2 Iced to 4°C Optional	6 months (Hg, 26 days)	Fill to shoulder of bottle	Shipped Daily by Overnight Carrier	No. 2 foam liner or vermiculite
Metals (leachate, surface water and private water supply wells)	One 1-liter high density polyethylene bottle	HNO ₃ to pH <2 Iced to 4°C	28 days	Fill to shoulder of bottle	Shipped Daily by Overnight Carrier	No. 2 foam liner or vermiculite
Cyanide	One 1-liter high density polyethylene bottle	NaOH to pH >12 Iced to 4°C	14 days	Fill to shoulder of bottle	Shipped Daily by Overnight Carrier	No. 2 foam liner or vermiculite
<u>Other Analysis</u>						
Chlorides, Alkalinity Sulfate	One 1-liter high density polyethylene	Iced to 4°C	28 days (14 days for alkalinity)	Fill to shoulder of bottle	Shipped Daily by Overnight Carrier	No. 2 foam liner or vermiculite
Total Organic Carbon, Ammonia, Nitrate-Nitrite, Chemical Oxygen Demand	One 1-liter polyethylene high density bottle	Iced to 4°C H ₂ SO ₄ to pH <2	28 days	Fill to shoulder	Shipped Daily by Overnight Carrier	No. 2 foam liner or vermiculite
Total Dissolved Solids Total Suspended Solids	One 1-liter polyethylene high density bottle	Iced to 4°C	7 days (filter upon receipt at lab)	Fill to shoulder	Shipped Daily by Overnight Carrier	No. 2 foam liner or vermiculite

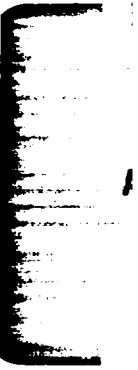
TABLE 4
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FOR WATER, SEDIMENT AND LEACHATE SAMPLES

<u>Analysis</u>	<u>Bottles and Jars</u>	<u>Preservation</u>	<u>Holding Time</u>	<u>Volume of Sample</u>	<u>Shipping</u>	<u>Normal Packaging</u>
<u>WATER AND LEACHATE</u>						
<u>Low Concentration (Organics)</u>						
Semi-Volatiles	Two (four for private wells) 1-liter amber bottle (teflon-lined cap)	Iced to 4°C	5 days until extraction, 40 days after extraction	Fill bottle to neck	Shipped Daily by Overnight Carrier	No. 1 foam liner or vermiculite
Pesticides/PCBs	Two (four for private wells) 1-liter amber bottle (teflon-lined caps)	Iced to 4°C	5 days until extraction, 40 days after extraction	Fill bottle to neck	Shipped Daily by Overnight Carrier	No. 1 foam liner or vermiculite
Volatiles	Two (three for private wells) 40-ml volatile organic analysis (VOA vials)	Iced to 4°C HCL to pH <2	7 days (48 hours for surface water)	Fill completely no headspace	Shipped Daily by Overnight Carrier	No.1 foam liner or vermiculite
<u>Low Concentration (Inorganics)</u>						
Metals (groundwater)	One 1-liter high density polyethylene bottle	Filter through 0.45 μ m filter, HNO_3 to pH <2 Iced to 4°C Optional	6 months (Hg, 26 days)	Fill to shoulder of bottle	Shipped Daily by Overnight Carrier	No. 2 foam liner or vermiculite
Metals (leachate, surface water and private water supply wells)	One 1-liter high density polyethylene bottle	HNO_3 to pH <2 Iced to 4°C	28 days	Fill to shoulder of bottle	Shipped Daily by Overnight Carrier	No. 2 foam liner or vermiculite
Cyanide	One 1-liter high density polyethylene bottle	NaOH to pH >12 Iced to 4°C	14 days	Fill to shoulder of bottle	Shipped Daily by Overnight Carrier	No. 2 foam liner or vermiculite
<u>Other Analysis</u>						
Chlorides, Alkalinity Sulfate	One 1-liter high density polyethylene	Iced to 4°C	28 days (14 days for alkalinity)	Fill to shoulder of bottle	Shipped Daily by Overnight Carrier	No. 2 foam liner or vermiculite
Total Organic Carbon, Ammonia, Nitrate-Nitrite, Chemical Oxygen Demand	One 1-liter polyethylene high density bottle	Iced to 4°C H_2SO_4 to pH <2	28 days	Fill to shoulder	Shipped Daily by Overnight Carrier	No. 2 foam liner or vermiculite
Total Dissolved Solids Total Suspended Solids	One 1-liter polyethylene high density bottle	Iced to 4°C	7 days (filter upon receipt at lab)	Fill to shoulder	Shipped Daily by Overnight Carrier	No. 2 foam liner or vermiculite

TABLE 4
(Continued)

<u>Analysis</u>	<u>Bottles and Jars</u>	<u>Preservation</u>	<u>Holding Time</u>	<u>Volume of Sample</u>	<u>Shipping</u>	<u>Normal Packaging</u>
<u>SOIL/SEDIMENT</u>						
<u>Low or Med Concentration (Organics)</u>						
Acid extractables, base/neutral extractables, pesticides/PCBs	One 8-oz wide mouth glass jar	Iced to 4°C	10 days until extraction	Fill 3/4 full	Shipped Daily by Overnight Carrier	Foam liner No. 3 (Med in cans/vermiculite)
Volatiles	Two 120-ml VOA vials	Iced to 4°C	10 days	Fill completely no headspace	Shipped Daily by Overnight Carrier	Vermiculite (Med in cans/vermiculite)
<u>Low or Med Concentration (Inorganics)</u>						
Metals and Cyanide	One 8-oz wide mouth glass jar	Iced to 4°C	6 months (14 days for cyanide)	Fill 3/4 full	Shipped Daily by Overnight Carrier	Foam liner No. 3 (Med in cans/vermiculite)
<u>Physical Analyses</u>						
Grain size, moisture content	One 8-oz wide mouth glass jar	None	not established	Fill 3/4 full	Shipped Daily by Overnight Carrier	Vermiculite
Atterberg Limits	One 8-oz wide mouth glass jar	None	not established	Fill 3/4 full	Shipped Daily by Overnight Carrier	Vermiculite
Permeability	3-in Shelby Tubes	4°C	not established	Fill 3/4 full	Shipped Daily by Overnight Carrier	Vermiculite
Total Organic Carbon	One 8-oz wide mouth glass jar	None	28 days	Fill 3/4 full	Shipped Daily by Overnight Carrier	Vermiculite

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APPENDIX A
SUPPLEMENTAL WORK PLAN
PHASE II RI/FS ACS SITE

**SUPPLEMENTAL WORK PLAN
PHASE II REMEDIAL INVESTIGATION
AMERICAN CHEMICAL SERVICES SITE
GRIFFITH, INDIANA**

INTRODUCTION

The original Scope of Work for conducting a Remedial Investigation/ Feasibility Study (RI/FS) at the American Chemical Services CERCLA Site, as developed for the Work Plan and approved in the consent agreement, specifies two phases of work for conducting the Remedial Investigation at the ACS Site. A majority of the Phase I work has been completed. This document represents a revised scope of work for conducting phase II of the Remedial Investigation.

In a memo dated October 17, 1989, Robert Swale, U.S. EPA Remedial Project Manager (RPM) proposed an expanded and revised scope of work for conducting Phase II of the RI. The PRP group has spent time and considerable expense during the month which followed Mr. Swale's memo, considering his proposal and responding to it. At the direction of the PRP group, Warzyn Engineering Inc. has drafted this Work Plan Addendum for Phase II RI tasks to respond to the U.S. EPA proposal.

Additional time and expense have been incurred by the PRP group, and the project has been delayed several weeks, while the PRPs have considered the U.S. EPA proposal, and in essence, re-negotiated a scope of work, modified from the one already approved in the signed consent agreement. That original work scope was developed in a joint effort among the U.S. EPA, EPA's technical contractor, Roy F. Weston, and Warzyn (representing the PRP group).

Warzyn has developed this Supplemental Work Plan (SWP) at the request of the PRP group to respond to the U.S. EPA Phase II proposal by re-organizing, modifying, and supplementing the previously-approved Phase II scope of work. If this SWP and associated QAPP addendum can be approved by December 6, 1989, it may be possible to initiate Phase II of the Remedial Investigation during the week of January 16, 1990. The project schedule has been revised for the assumed January 16, 1990 start of Phase II; it is included as Table 1.

PROPOSED PHASE II SCOPE OF WORK ACS CERCLA SITE

The following description of activities for the Phase II Remedial Investigation at the ACS CERCLA site is organized in the sequence of the U.S. EPA's October 17, 1989, "Proposal for Phase II of the RI/FS" to facilitate review. The field and sampling activities for each of the activities are summarized in Table 2.

A. GROUNDWATER AND SURFACE WATER FLOW DIRECTION

Four monitoring wells will be constructed during Phase II with screens sealed in the lower aquifer. Water levels from these wells will provide data to calculate groundwater flow direction in the lower aquifer. Water levels collected at these lower aquifer wells will be analyzed with the data base which includes water levels at the Phase I monitoring wells, piezometers, and staff gages. The results will be used to document the vertical hydraulic gradient between the upper and lower aquifer across the site. Water levels will also be used to document horizontal gradients in the lower aquifer.

Water levels have been measured at all piezometers, monitoring wells, and staff gages on two dates. Two additional measurements will be made during Phase II of the investigation: one during December 1989/January 1990 when the ground is frozen, and the second during March/April 1990, when the annual hydrograph is expected to be at its peak. Up to four additional water level measurements will be made at a representative group of measuring points (8-12 of the piezometers, monitoring wells, and staff gages), to provide more detailed data regarding interactions between groundwater and surface water, and response to aquifer stresses.

Existing geologic and hydrogeologic information will be evaluated and used to supplement the results of Phase I and II site investigations. Sources include: information in U.S. EPA files, and the Preliminary Hydrogeologic Site Assessment conducted in January 1986 by ATEC Associates for Mr. James Tarpo. The ATEC report contains boring logs, sampling information and water level data from 1986.

A numerical model will be used to synthesize the climatological data, aquifer characteristics data, and water level data into a conceptual flow model. This will be useful in developing an understanding of the groundwater flow system and its interactions with surface water, and in evaluating potential remedial alternative scenarios.

B. CONTAMINANT PLUME DELINEATION

Upper Aquifer Investigation. Four to eight Phase II monitoring wells are specified in the approved work plan. Water level measurements in the upper aquifer indicate that there is a groundwater high beneath the ACS Inc. facility, and that groundwater flow may be radially outward. Therefore it is possible that the groundwater plume extends in several directions from the site.

With the potential for a plume to extend in all directions from the site, it is uncertain whether the plume could be adequately delineated if the only further activity is installing eight additional monitoring wells. Therefore, it will be cost effective to use a field screening technique to optimize the locations and limit the number of monitoring wells. Soil gas sampling is a generally accepted field screening technique. However, it appears that the field work will be conducted in the winter when ground will be frozen so there may be potentially high volatile organic concentrations in the ambient air and there may be a high potential of getting meaningless results.

An effective field screening method at the ACS site would be to collect groundwater samples at multiple locations surrounding the site to be analyzed for VOCs or semivolatile compounds. The water levels measured at the piezometer network have provided precise data regarding the depth to the water table, so it would be relatively efficient to penetrate through the water table and collect a groundwater sample for field GC analysis. The result would be an analytical test result for the groundwater at the sampled location.

It is proposed that Tracer Research Corporation (Tracer) be subcontracted to collect water samples from the aquifer in the zones indicated in Figure 1. Tracer uses a sampling van with the capability of driving a sampling probe into the ground to collect a groundwater sample. After the water sample is collected, head space analysis is

conducted using the field GC instrumentation in the van. Using this method, it will be possible to map the extent of the VOC plume in the upper aquifer in two or three days. On the basis of the field screening, the well locations will be selected to intersect the outer edge of plume in the upper aquifer, thereby documenting its extent and character. Locations and numbers of wells (up to maximum of eight) necessary to adequately accomplish this goal will be determined from the field screening results.

Aquifer samples (solid matrix samples) will be collected at up to five points within the groundwater contamination plume to provide an indication of contaminant characteristics for remedial alternatives evaluations. The locations will be determined from the field screening results. Parameters for analysis will be VOC and semi-volatile organic compounds.

Lower Aquifer Investigation. The January 1986 Preliminary Hydrogeologic report by ATEC describes a monitoring well constructed in the lower aquifer in 1985. The report indicates that the clay layer is approximately 12 feet thick at the ACS facility, located between elevations 603 and 615 feet mean sea level.

During Phase II, four monitoring wells will be constructed in the lower aquifer to provide hydraulic gradient and water quality information. A double casing drilling technique will be used to avoid potential cross-contamination from the upper aquifer. The wells will be constructed with stainless steel materials, and will have five-foot screens located in the upper zone of the lower aquifer. The first three lower aquifer wells will be constructed at the approximate locations indicated on Figure 2. The fourth well location will be selected to be downgradient of the site on the basis of water levels in the first three.

Groundwater Sampling. The approved work plan specifies that two rounds of sampling will be conducted at each Phase I and Phase II monitoring wells. The target compound list (TCL) of organic parameters and the target analyte list (TAL) for inorganic parameters will be tested for in the first round of sampling at each well. For the second round of sampling at each well, the parameter list may be reduced to test for only the groups of compounds which were indicated in the first round of sampling.

During Phase II, the second round sampling will be conducted at the Phase I wells (MW-1 through MW-6), and both rounds of sampling will be conducted in the Phase II wells. The parameter list for Phase I monitoring wells has been reduced on the basis of Phase I sampling results to include VOCs and semivolatile compounds.

Provided access can be obtained, ten existing water supply wells within one mile of the site will be sampled. Water levels measured in the four lower aquifer monitoring wells will be used to determine the groundwater flow direction in the lower aquifer in the vicinity of the site. Nine downgradient locations and one upgradient location will be selected for sampling and samples will be analyzed for TCL and TAL parameters.

Additional efforts will be made to classify the general characteristics or groupings of the groundwater sampling results which have been classified as "unknown" compounds in Phase I sampling results.

C. AQUIFER TESTS AND ENGINEERING EVALUATION

The purpose of conducting aquifer tests in the Remedial Investigation is (1) to provide an adequate characterization of aquifer characteristics to evaluate potential fate and transport of contaminants for the Endangerment Assessment and (2) to provide scoping information for remedial alternatives evaluation in the Feasibility Study.

Aquifer tests were conducted by bail test at each of the Phase I monitoring wells. In addition, grain size analysis was conducted on samples from the aquifer material collected from the screened zone of each of the six monitoring wells. The aquifer tests indicate that the hydraulic conductivity (K) in the upper aquifer ranged between 1.5×10^{-3} cm/sec at MW-2 where the aquifer consisted of fine sand, to 1.2×10^{-2} cm/sec at MW-5, where the aquifer material consisted of sand and gravel.

These results indicate the bail tests, supplemented with grain size analyses, have been adequate to characterize the aquifer properties at the ACS site. There is no indication that conducting a pumping test would provide significantly more precise aquifer data. It is likely that conducting a pumping test would cause delays in project progress because the water pumped during a pumping test would be contaminated. Warzyn's experience

indicates that it would be very difficult and time consuming to obtain permits for disposal of the pumped groundwater.

The physical and chemical characteristics of the three major geologic units will be further characterized by additional analyses. Two soil samples will be collected from the upper aquifer (Calumet Aquifer), the confining clay layer, and the lower aquifer (Valparaiso Aquifer). Analyses for each of the six samples will include (as appropriate): grain size, Atterberg Limits, total porosity, and total organic carbon (TOC).

A groundwater flow model will be used to synthesize the slug test data, climatological data, and the water level measurements, and develop a conceptual model of the upper aquifer flow regime.

D. FURTHER CHARACTERIZATION OF SITE STRATIGRAPHY

Eight to twelve additional borings will be made to install monitoring wells during the Phase II investigation. Four of the borings will extend through the clay confining layer and be completed as double cased lower aquifer monitoring wells. The results of these boring will document the total thickness of the clay confining layer at different locations beneath the site.

Each of the four lower aquifer wells will be constructed in the vicinity of an upper aquifer monitoring well to create "well nests" at four diverse locations across the site. Water levels measured both above and below the confining layer at each of these locations will provide further data to evaluate the integrity and continuity of the clay layer throughout the site. Additional information regarding physical properties of each geologic unit will be obtained in Activity C.

E. DELINEATION OF SURFACE WATER/SEDIMENT CONTAMINATION

The approved Work Plan specified 1 surface water and 1 sediment sample at 11 locations (22 total samples) for the Phase I investigation. During the field activities, there was no standing water at several of the Surface Water/Sediment (SW/SD) sampling locations. Mr. Swale agreed that collecting sediment samples only at these locations would sufficiently characterize the conditions. As a result, the samples which were not collected in Phase I will be re-allocated to Phase II.

Five sediment sampling locations have been identified to further characterize the surficial contamination in the adjacent surface water areas and drainageways surrounding the site and along the railroad between the Griffith Landfill and the marshy area to the north. General locations are shown on Figure 3.

To aid in the determination of the sorptive properties and natural attenuation capabilities of the wetland soils, six near surface soil samples will be collected and submitted for laboratory analysis. Characteristics tests will include grain-size analysis and total organic carbon (TOC) determination.

F. WETLANDS DELINEATION

During November 1989, aerial photographs were taken of the ACS site and surroundings. Besides the photography to develop the site base map (1 in = 100 ft, 2-ft contour interval), a black and white photograph and a color infrared photograph were taken. Initial wetland delineation may be conducted through interpretation of these photo maps.

U.S. EPA has reported that there is an interest by the Fish and Wildlife Department, Indiana agencies, and local interest groups, to have detailed wetlands assessment conducted. Apparently, the Fish and Wildlife Department has scheduled site work for the spring of 1990. The PRP group will discuss the requirements of the assessment with the appropriate agencies before the work is scheduled to begin, and develop an approach to avoid duplication of effort.

G. TREATABILITY STUDIES

Phase I findings indicate that there are no wastes or contamination problems which have not been encountered previously at other CERCLA sites. Therefore, there should be existing information from other sites to evaluate the treatability without conducting detailed treatability studies with ACS waste.

To facilitate completion of the feasibility study, it is appropriate to collect some additional data regarding the chemical and physical properties of the contaminated site media. The media which will require remediation are: the soil/waste and the groundwater.

The purposes of Phase II soil/waste sampling are to further delineate the extent of waste (Activity H) and to characterize chemical and physical properties of the waste for compatibility and treatability. Field observations during Phase I indicate that the waste characteristics are highly diverse. The Work Plan specifies that appropriate test parameters may be selected for each sample. Therefore, field decisions will be made to perform appropriate analyses for characterizing waste compatibility and treatability. Examples of possible test parameters are total organic carbon, BTU rating, and potential ash generation.

Most of the laboratory analyses which might be useful in assessing groundwater treatability are being conducted in the TCL and TAL sampling required in Round 1 of the sampling. Several field measurements will be conducted during Phase II field work including: pH, temperature, dissolved oxygen, redox potential, depth to groundwater, and saturated thickness.

After the feasibility study is completed, and a final design has been selected, it may be appropriate to conduct bench or scale studies to appropriately scope the final remedy.

H. ADDITIONAL WASTE BURIAL DELINEATION AND CLOSING OF DATA GAPS

The approved Work Plan specifies that 20 additional solid matrix samples will be collected during Phase II to further delineate the vertical and horizontal extent of soil/waste contamination at the site. In addition, 10 samples designated for collection in Phase I were not collected. These include the six surface water samples discussed in Activity E (above), and four surface area (SA) samples which were deferred during the Sample Location Staking, conducted on June 15, 1989. (During location staking, representatives of U.S. EPA, U.S. EPA's consultant, and Warzyn agreed to defer surface area samples which were either redundant to other sampling locations, or were located in high traffic areas). Since these samples were Phase I samples, they included the full TCL and TAL parameter list.

As a result, a total of 30 solid matrix samples remain to be collected from the total number of solid matrix samples designated for Phase I and II of the approved work plan. Five of these samples have been allocated to the sampling surface sediment in Activity E above. Another five have been allocated to characterizing the interior upper aquifer

contaminant plume (Activity B).

The remaining 20 sampling locations will be assigned to delineate the extent of contamination in known waste areas, and to characterize and delineate waste in newly identified areas. The most flexibility will result by conducting the soil/waste sampling following the procedure used in Phase I.

The Phase I procedure was to delineate the horizontal and vertical extent of buried waste using auger probes; then, to go back to areas which the auger probes indicated were most highly contaminated, or most characteristic of a given area, and collect samples. This procedure will be used in four areas (indicated on Figure 4):

- A zone between the Kapica area and the Griffith Landfill
- A zone between the Kapica area and the Off-Site Containment Area
- The Off-Site Containment Area
- The area west of the existing treatment lagoon

Auger probes will be used as a field screening method in each area to develop visual and field instrument characterizations of the waste types and the horizontal and vertical extent. Then 20 Phase II solid matrix samples will be used to characterize the waste for compatibility and treatability as appropriate.

I. ENVIRONMENTAL AUDIT OF THE AMERICAN CHEMICAL SERVICES FACILITY

The work scope for Phase I of the RI included an environmental audit of the ACS facilities. After a lengthy delay in providing site access to conduct the audit, ACS Inc. management allowed the audit to proceed during the week of November 13, 1989.

Tables

1. Schedule for Implementation of Phase II Activities
2. Summary of Additional or Modified Data Generating Activities

Figures

1. Field Screening Areas
2. Proposed Locations for First Three Lower Aquifer Wells
3. Surface Sediment Sampling Areas
4. Waste Areas Requiring Further Delineation

V251QAPP2PJV/dms/gmg/JDA

TABLE 1

SCHEDULE FOR IMPLEMENTATION AND PHASE II ACTIVITIES
AMERICAN CHEMICAL SERVICES SITE
REMEDIAL INVESTIGATION

<u>Date</u>	<u>Event/Deliverable</u>
January 16, 1990	Supplemental Work Plan and QAPP Addendum Approval
January 22, 1990	Phase II Mobilization
March 5, 1990	Completion of Phase II Monitoring Wells
March 23, 1990	Completion of Phase II Field Work
June 4, 1990	Complete validation of Phase II, Round 1 samples
April 13, 1990	Completion of Phase Round 2 groundwater sampling
June 19, 1990	Complete validation of Round 2 groundwater samples from Phase II wells
June 25, 1990	First Draft Remedial Investigation Report Submitted to U.S. EPA

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Table 2

**Summary of Additional or Modified Data Generating Activities
And Associated Data Quality Objectives
American Chemical Services Site**

<u>Activity</u>	<u>Supplemental Work Plan Reference Letter</u>	<u>Use of Data</u>	<u>Data Quality Objectives</u>
Private Well Sampling	B	Examine potential contamination of private water supply wells surrounding the site.	Identify compounds present. Meet performance criteria for TCL organics as stated in CLP SOW 7/87 (or most recent). Meet performance criteria for inorganics and indicators as specified in Appendix F. of original QAPP and Appendix C of QAPP Addendum.
Upper Aquifer Field Screening	B	Aid in identification of horizontal extent of ground-water contamination by VOCs for monitoring well placement.	Estimate concentrations (;50%) of BETX compounds as indicators of VOC contamination. Meet performance criteria specified in Appendix B-3 of QAPP Addendum.
Field Parameter Analysis (D.O. and Redox)	G	Aid in assessing treatability	Meet instrument performance criteria specified in Appendix B-4 and B-5.
Sediment Sampling	E	Determine sorptive properties and natural attenuation capabilities of wetlands.	Meet performance criteria for grain size specified in Appendix F of original QAPP and criteria for TOC specified in Appendix B-2 of QAPP Addendum.

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SUPPLEMENTAL WORK PLAN
PHASE II REMEDIAL INVESTIGATION
AMERICAN CHEMICAL SERVICES SITE
GRIFFITH, INDIANA

WALSH ENGINEERING INC.
Madison • Milwaukee
Minneapolis • Chicago
Detroit

Approved By RH

Date 11/22/19

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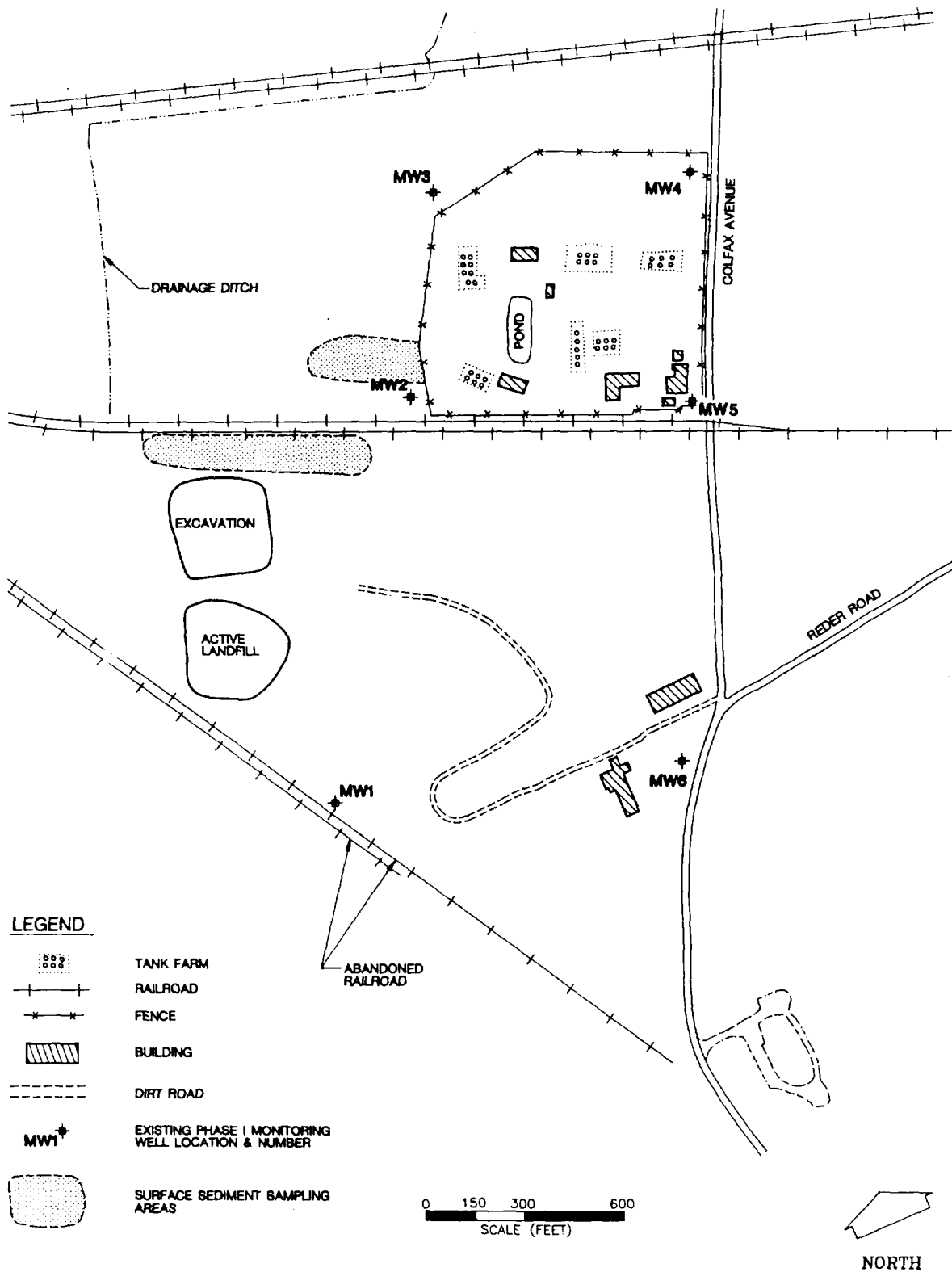


FIGURE 3

	SURFACE SEDIMENT SAMPLING AREAS SUPPLEMENTAL WORK PLAN PHASE II REMEDIAL INVESTIGATION AMERICAN CHEMICAL SERVICES SITE GRIFFITH, INDIANA	Date: By: App:	WARZYN 6025108	Designed By: RV Drawn By: ELR Checked By: TWP Approved By: [Signature] Date: 11/19/89
	OF	6025108	6025108	6025108
	6025108	6025108	6025108	6025108
	6025108	6025108	6025108	6025108

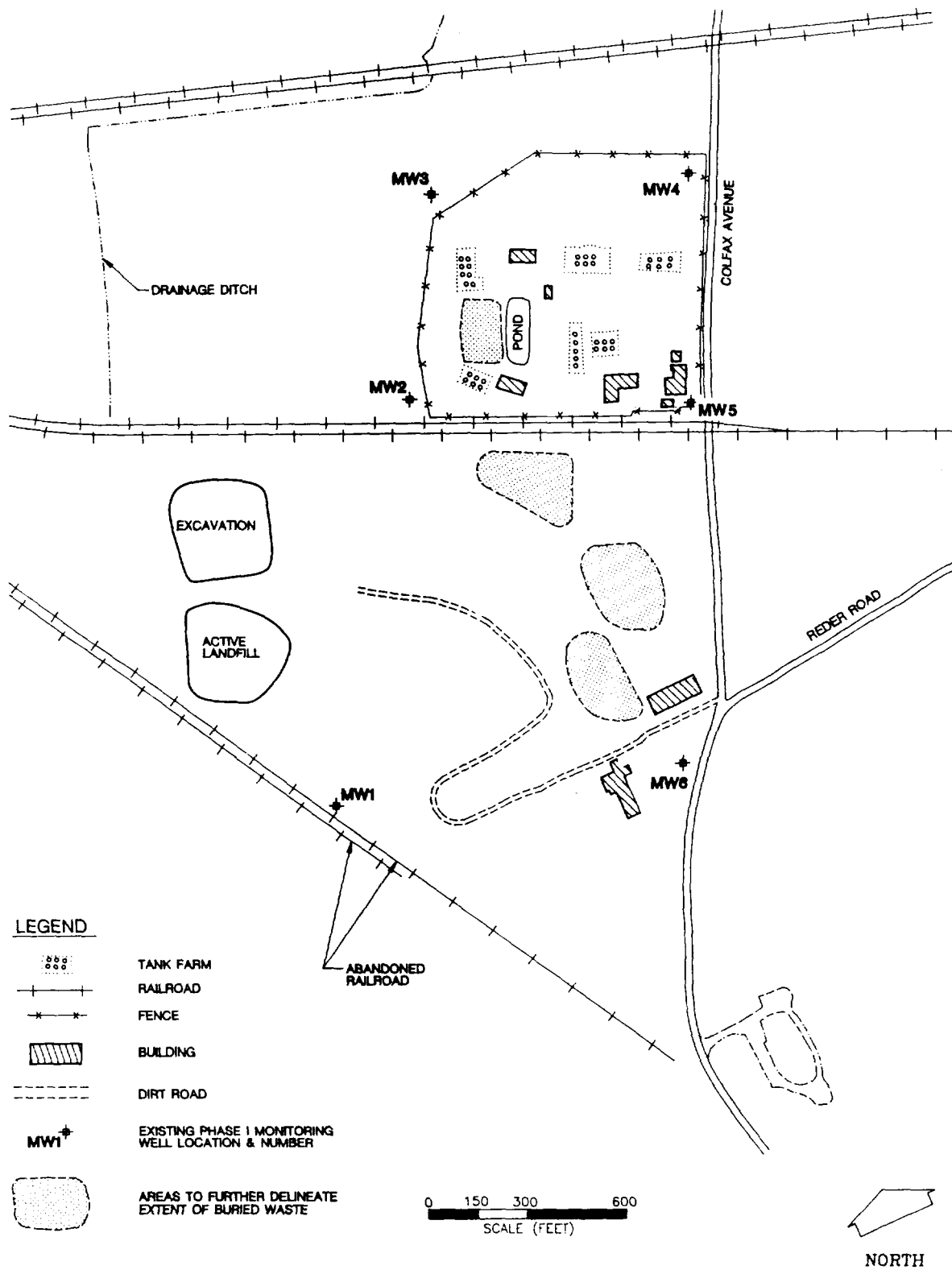


FIGURE 4

	WASTE AREAS REQUIRING FURTHER DELINEATION SUPPLEMENTAL WORK PLAN PHASE II REMEDIAL INVESTIGATION AMERICAN CHEMICAL SERVICES SITE	Date: 11/20/81 By: [Signature]	WARZYN WARZYN & COMPANY, INC. Milwaukee - Minneapolis Morrisville - Chicago Dallas	Designed By: [Signature] Drawn By: [Signature] Checked By: [Signature] Date: 11/20/81
	OF	60251.00	0	0
	0	0	0	0
	0	0	0	0



B

APPENDIX B-1

**LOW DETECTION LIMIT METHODS FOR ORGANIC ANALYSIS
OF PRIVATE WELL SAMPLES**

STANDARD OPERATING PROCEDURE

LOWER DETECTION LIMIT LIQUID

VOLATILE ORGANICS

STANDARD OPERATING PROCEDURE

OVERVIEW:

This method is for the analysis of EPA or COMMERCIAL HSL Lower Detection Limit liquid samples. All standards, blanks, samples and other required runs must be injected within twelve (12) hours of the time the BFB was injected. All injections must be recorded in the instrument log including the date, time (use a twenty-four hour time scale), volume injected, operator ID, disk number, and any comments relevant to the injection. At the end of the tune, unused run lines must be x'd out by the operator and the log page signed and dated by the operator. One copy of the log page should be placed in the log book and the other attached to the standard package for that tune.

ORDER OF ANALYSIS:

1. BFB.

All criteria must be met according to requirements established by the EPA (See SOP for BFB tuning). Approved tunes must have the operator's initials in the blank labeled "Data Released By".

2. CONTINUING CALIBRATION CHECK STANDARD.

If the instrument has a valid multipoint and the calibration check standard meets all requirements then it may be used for the tune.

3. MULTIPOINT.

If the instrument does not have a valid multipoint for this analysis or if the calibration check standard does not meet all required criteria then a five-point calibration must be run. The five-point calibration must meet all criteria as established by the EPA.

4. 25 ML CONTINUING CALIBRATION CHECK STANDARD.

If the instrument has a valid multipoint and the calibration check standard meets all requirements, then a 25 ml, 10 ug/l continuing calibration check standard is analyzed. All data is quantitated using the response factors from this standard.

5. 25 ML INSTRUMENT BLANK.

All surrogate criteria must be met. All compounds must be BDL (below detection limits) except for methylene chloride and acetone. Methylene chloride and acetone may be present at up to the detection limit in the first blank and up to twice the detection limit in the second blank, if the concentrations in the

two blanks are comparable. A valid blank must be obtained before any samples may be analyzed. If no samples are analyzed during a "tune", a valid blank is still required if a multipoint has been run.

6. SAMPLES.

All samples must be injected within twelve (12) hours of the time the BFB was injected. Samples should be analyzed according to batch and due date. Any other required injection, such as quarterly proficiency tests, sample spikes, blank spikes, etc. must also be analyzed during this time.

FIVE-POINT CALIBRATION

FREQUENCY:

A five-point calibration must be performed if the instrument does not have a valid multipoint for this method or if the calibration check standard fails to meet all required criteria (established by the EPA).

NOMINAL CONCENTRATION VALUES:

The nominal concentration values and standard ID's for the five-point calibration are as follows.

STANDARD ID	CONCENTRATION (ug/l)
1859	200
1858	150
1857	100
1856	50
1855	20

STANDARDS PREPARATION:

Standards are prepared for any given level by using the volumes listed below. All standards are prepared by spiking the appropriate volume of each standard solution into gas tight syringes containing 25mls of sparged, distilled/deionized water. All primary analytical standards should be stored in the volatile standards refrigerator when not in use. (All volumes are given in ul).

STANDARD ID #	1855	1856	1857	1858	1859
036	5.0	5.0	5.0	5.0	5.0
394	5.0	5.0	5.0	5.0	5.0
1301	1.0	2.5	5.0	7.5	10.0
1307	1.0	2.5	5.0	7.5	10.0
1322	1.0	2.5	5.0	7.5	10.0

STANDARDS ANALYSIS:

Immediately after the standards are prepared they are injected via the teflon stopcock on the Tekmar into the purge vessel and purged for twelve (12) minutes. Samples are analyzed using the AC program in the form

AC filename # number of scans to acquire

Enter the appropriate information for sample description, including instrument ID and operator ID (as prompted by the program). When the information has been entered and the instrument is ready, the Tekmar is switched to the desorb position and the

sample is introduced onto the head of the column. The data acquisition will continue unsupervised until the designated number of scans has been acquired. Enough scans should be acquired so that the final compound completely elutes.

QUANTITATION:

Standards are quantitated using the RK program with option 2. The RK procedure allows individual compounds to be quantitated using an average fit to the response list of the most recently updated continuing calibration check standard for the particular analysis. The RK procedure is initiated by typing the command in the form

RK filename #2, linker

where the linker for standards quantitation is E237. All forty-two (42) compounds must be found for each standard in the five-point calibration. Compounds not found by the RK program can be found by the UPQUAN program in the form

UPQUAN library ID # library entry

After all compounds have been found, the quantitation list must be edited. This can be accomplished using the EQL program in the form

EQL filename , filename

and deleting any blank entries on the quantitation list. When the quantitation list has been edited, it must be sorted using the QSORT program in the form

QSORT filename , linker

where the linker is E237 for standards quantitation. The quantitation list can then be reprinted by the MQ program in the form

MQ filename ;F2;H;E

which will print the compound list and the F2 table. If a large number of compounds were not found by the RK program, then at this point the 11 table should be updated so that the compounds in subsequent samples will be located correctly. This can be accomplished by typing the following commands:

SET1 filename
SET2 linker
RKSL B'1E

To enter these commands, you must be in the Alternate Executive mode of the computer. If you are not in the Alternate Executive mode, typing DISSW will put you into this mode. After entering the above commands and updating the 11 table, you should again type DISSW to return you to the normal operating mode.

GENERATING THE MULTIPOINT:

After all five standards have been quantitated, the multipoint is generated using the EPAMP program in the form

EPAMP linker

where the linker is E237. The program will then prompt you to enter the filenames of the low, med-low, med, med-high, and high level standards. The EPAMP program will then generate a report detailing the response factors for each standard, the average response factor for all five standards, and the percent relative standard deviation (RSD) for each compound. If the response factor for one or more compounds is missing then the multipoint will be incorrect. The appropriate standard must be corrected using the above procedures and the EPAMP program run again. Compounds designated as SPCC and CCC must also meet the EPA multipoint criteria (see SPCC and CCC criteria below). In addition, the multipoint must be inspected for any bad entries or unusual data points. This multipoint is double checked and approved by either a Senior Operator or the Data Review Specialist.

DEFINITION OF A VALID MULTIPOINT:

1. One (1) valid injection of each of five standard concentrations.
2. All standards acquired under a valid tune.
3. All compounds present in all five (5) standards.
4. All isomer pairs must be resolved.
5. All SPCC criteria must be met.
6. All CCC criteria must be met.
7. A valid Instrument Blank obtained.
8. Multipoint reviewed and signed off by Senior Operator/Data Review Specialist.
9. Spectra of any hits in the blank.
10. Searches of any extraneous peaks in the blank RIC.

SPCC CRITERIA:

The following compound must have an average response factor greater than or equal to 0.300 in the multipoint.

Chloromethane
1,1-Dichloroethane
Bromoform (0.250 for Bromoform only)
1,1,2,2-Tetrachloroethane
Chlorobenzene

CCC CRITERIA:

The following compounds must have a percent RSD (between the five standards) of less than or equal to 30% in the multipoint.

Vinyl Chloride
1,1-Dichloroethylene
Chloroform
1,2-Dichloropropane
Toluene
Ethylbenzene

CONTENTS OF THE MULTIPOINT PACKAGE:

A complete multipoint package must contain each of the following:

1. BFB tuning and mass calibration forms.
2. A quantitation report form for each standard.
3. A labeled RIC for each of the five standards.
4. The Multipoint form generated by the EPAMP program.
5. A quantitation report form for a valid blank.
6. A labeled RIC for the instrument blank.
7. A compound list for the instrument blank which also provides surrogate information.
8. Internal Standard Monitor for blank.

CONTINUING CALIBRATION CHECK STANDARD

FREQUENCY:

A Calibration Check Standard should be run immediately after the SFE is injected. If there is no valid multipoint on the instrument, then a Calibration Check Standard must be run after a valid multipoint has been obtained. A valid Calibration Check Standard must be obtained before any samples can be analyzed.

NOMINAL CONCENTRATION:

50 ug/l

No substitution of standard concentration is allowed.

CALIBRATION CHECK STANDARD PREPARATION:

The Calibration Check Standard is prepared by injecting the following amounts of the primary analytical standards into a 5 ml gas tight syringe containing 5 ml of sparged, distilled/deionized water. All volumes are given in ul.

STANDARD ID #	
	1856
036	5.0
394	5.0
1301	2.5
1307	2.5
1322	2.5

STANDARD ANALYSIS:

The Calibration Check Standard is analyzed according to the procedure defined under the Five-Point Calibration.

QUANTITATION:

The Calibration Check Standard is quantitated according to the procedure defined under the Five-Point Calibration.

CHECK STANDARD CALIBRATION FORM:

The validity of the calibration check standard is checked using the EPAUP program in the form

EPAUP filename . linker .

where the appropriate linker for the analysis is used. This program sets the library amounts correctly, updates the 11 table*, and prints the continuing calibration form. This form lists the percent difference in the response factors in the shift standard and the response factors in the multipoint. The Calibration Check Standard must meet all SPCC and CCC requirements (below) as established by the EPA or a new five-point calibration must be run.

*Since this program updates the 11 table, the appropriate linker must be used.

SPCC CRITERIA:

The following compounds must have an average response factor greater than or equal to 0.300 in the multipoint.

- Chloromethane
- 1,1-Dichloroethane
- Bromoform (0.250 for Bromoform only)
- 1,1,2,2-Tetrachloroethane
- Chlorobenzene

CCC CRITERIA:

The following compounds must have a percent RSD of less than or equal to 25% in the multipoint.

- Vinyl Chloride
- 1,1-Dichloroethylene
- Chloroform
- 1,2-Dichloropropane
- Toluene
- Ethylbenzene

25 ML CONTINUING CHECK STANDARD

FREQUENCY:

The 25 ml Continuing Check Standard should be run immediately after the 5 ml, 50 ug/l Continuing Calibration Check Standard.

NOMINAL CONCENTRATION:

10 ug/l

No substitution of standard concentration is allowed.

25 ML CONTINUING CHECK STANDARD PREPARATION:

The 25 ml Continuing Check Standard is prepared by injecting the following amounts of the primary analytical standards into gas tight syringes containing 25 ml of sparged, distilled/deionized water. All volumes are given in ul.

STANDARD ID #	AMOUNT
036	5.0
394	5.0
1301	2.5
1307	2.5
1322	2.5

STANDARD ANALYSIS:

The 25 ml Continuing Check Standard is analyzed according to the procedure defined under the Five-Point Calibration.

QUANTITATION:

The 25 ml Continuing Check Standard is quantitated according to the procedure defined under the Five-Point.

UPDATING THE 25 ML CONTINUING CHECK STANDARD:

The 25 ml Continuing Check Standard is updated by using the UPLIB program to change the amounts in the libraries to 10. This is done by following the prompts after typing

UPLIB E237

and then going into the MQ program, paging through all of the compound names, and typing

RtE

This will update your response list. In order to update the internal standard monitor one types

SAVSTD FILENAME,LINKER

CONTENTS OF THE STANDARDS PACKAGE:

The complete standard package must contain each of the following .

1. BFB tuning and mass calibration forms.
2. A quantitation report form for the Check Standard.
3. A labeled RIC for the Calibration Check Standard.
4. The Check Standard Calibration Form generated by EPAUP.
5. A quantitation report for the 25 ml Check Standard.
6. A labeled RIC for the 25 ml Check Standard.
7. A quantitation report form for a valid blank.
8. A labeled RIC for the instrument blank.
9. A compound list for the instrument blank which also provides surrogate information.
10. Internal Standard Monitor for blank.
11. Spectra of any hits in the blank.
12. Searches of any extraneous peaks in the blank
RIC:

25 ML INSTRUMENT BLANK

FREQUENCY:

A valid 25 ml blank must be obtained to go with a valid BFB run, a valid check standard, and a 15 ml check standard.

25 ML INSTRUMENT BLANK PREPARATION:

A 25 ml instrument blank is prepared by filling gas tight syringes with 25 mls of water. To this volume 5 ul of Internal Standard #036 and 5 ul of Surrogate #394 are added.

25 ML INSTRUMENT BLANK ANALYSIS:

The 25 ML Instrument Blank is analyzed according to the procedure under Sample Analysis.

QUANTITATION:

The 25 ml Instrument Blank quantitation is analyzed according to the procedure under Sample Quantitation.

GENERATION OF THE COMPOUND LIST:

The 25 ml Instrument Blank Compound List is generated following the procedure under Sample Generation Of The Compound List.

GENERATION OF SPECTRA:

The dual spectra and comparative spectra of any compounds found can be generated by typing

QLL6V

LIBRARY SEARCHES:

The 25 ml Instrument Blank Library Searches are generated following the procedure under Sample Library Searches.

Documentation Form For:

Revising or Creating Standard Operating Procedures (SOPs): Including Designated Personnel Responsibilities

 Revised Procedure ✓ New Procedure ✓ Procedure Attached

GC IP 152: LDL; Water; Pesticide/PCBs (Res. Well) 10-28-88
Procedure Area, Title, and SOP Number Effective Date

Doug M. Cormack 4-3-88
Procedure Prepared By Date

Doug M. Cormack 4-7-89
Procedure Read, Understood, and Approved By Date
Appropriate Laboratory Station Manager,

Robert E. Mueen 10/23/89
Procedure Read, Understood, and Approved By Date
Quality Assurance Representative

This procedure(s) meets the requirements as set forth in the following
References for Approved Methods:

F: USEPA Contract Laboratory Program, Statement of Work
for Organic Analysis, Multi-Media, Multi-Concentration,
2/88, Region 5 SAS

These procedures describe how tasks are performed in this specific area.
If a question arises concerning the proper procedure to follow for an activity
in this area, these SOPs should be consulted to resolve the question. Also,
these SOPs are a valuable source of material for training purposes.

After the manager of this area believes the person responsible for these
tasks has mastered these SOPs, both the manager and the employee should sign and
date this form, assuring that these SOPs are understood and will be followed in
the daily operations of CompuChem Laboratories. Please forward a copy of this
revised or created SOP and a completed form to Quality Assurance.

Employee's name: _____ Date: _____

Employee's title: _____

Employee's name: _____ Date: _____

Employee's title: _____

Manager's name: _____ Date: _____

Manager's title: _____

INSTRUMENT PROCEDURE: Reswell Lower Detection Limit Water
Instrument Code 410

Principle, Scope, Application:

This method, which follows USEPA CLP Statement of Work 2/88, is applicable for the analysis of samples requiring Reswell EPA Region V lower detection limit method for volatile organic compounds by the purge and trap method using a Finnegan OWA GC/MS, column DB624 (30 m.). All standards, blanks, samples and other required runs must be injected within twelve (12) hours of the time the valid BFB analysis was started. All injections must be recorded in the instrument log including the date, time (using a military time), volume injected, operator I and any comments relevant to the injection. At the end of the tune unused run lines must be Xed out by the operator and the log page signed and dated by the operator. One copy of the log page should be placed in the log book and the other attached to the standard package for that tune.

Parameters

Refer to Attachment #1 for a list of target analytes, CAS #s, and quantitation limits.

ORDER OF ANALYSIS:

BFB ---> Initial Calibration ---> BFB ---> Continuing Calibration --->
Instrument Blank ---> Samples
1. BFB.

All criteria must be met according to the requirements established by the EPA. GC/MS Tuning and Mass Calibration forms must be printed by the instrument. All relative abundance calculations are displayed according to the requirements of the 02/88 Organic Statement of Work with current revisions.

BFB KEY IONS AND ABUNDANCE CRITERIA

<u>Mass</u>	<u>Ion Abundance Criteria</u>
50	15.0 - 40.0 percent of base peak
75	30.0 - 60.0 percent of base peak
95	base peak (100 percent relative abundance)
96	5.0 - 9.0 of base peak
173	< 2.0 percent of mass 174
174	greater than 50 percent of the base peak
175	5.0 - 9.0 percent of mass 174
176	> 95.0 percent and < 101.00 of mass 174
177	5.0 - 9.0 percent of mass 176

A valid tune is defined as encompassing all injections made within twelve hours from the injection time of a valid BFB analysis.

2. Continuing Calibration

If the instrument has an acceptable current Initial Calibration Standard for analysis code 410 and the calibration check standard meets all requirements then samples may be analyzed and quantitated against the calibration check standard.

3. Initial Calibration.

If there is no current Initial Calibration for analysis code 410 or if the calibration check standard fails to meet all SPCC and CCC requirements then a new 5 point calibration must be created. The 5 point calibration must meet all criteria established by the US EPA. Prior to the analysis of samples against the new Initial Calibration a continuing calibration check standard must be analyzed and all continuing calibration and system performance criteria must be met.

4. Instrument Blank.

A valid instrument blank must be obtained prior to the analysis of any sample. For a definition of a valid instrument blank see the section on instrument blanks.

5. Samples

All samples must be injected under a valid BFB tune. Samples should normally be analyzed according to batch and due date. Sample spikes, blank spikes and any required QC will be treated as samples. For further information see the section on sample analysis and work-up.

FIVE POINT CALIBRATION

Frequency:

A five-point calibration must be performed if:

1. There is no current calibration available for the instrument or,
2. The continuing calibration standard fails to meet either 1) one or more of the Calibration Check Compound criteria or the 2) one or more System Performance Check Compound criteria as established by the US EPA.

Nominal Concentration Values:

The nominal concentration values and standard ID's for the five-point calibration are as follows.

STANDARD ID	CONCENTRATION -(ug/l)
1896	5.0
1897	10.0
1898	20.0
1899	40.0
1900	60.0

STANDARDS PREPARATION:

Standards are prepared for any given level by spiking the appropriate volume of each standard solution into a 10 ml gas tight syringe containing 10 ml of sparged, distilled/deionized water. Another 10 ml syringe is filled with sparged distilled/deionized water at the time of standard preparation to be added to the purge vessel to bring the standard volume to 20 ml. All analytical standards are stored in mininert vials with a minimum of headspace in a four (4) degree C refrigerator used solely for the storage of analytical standards.

STANDARD ID #	5.0 ug/l	10.0 ug/l	20.0 ug/l	40.0 ug/l	60.0 ug/l
	1896	1897	1898	1899	1900
	(ul)	(ul)	(ul)	(ul)	(ul)
(IS) 036 (20 ug/l)	8.0	8.0	8.0	8.0	8.0
(Surr)394 (20 ug/l)	8.0	8.0	8.0	8.0	8.0
1301	1.0	2.0	4.0	8.0	12.0
1307	1.0	2.0	4.0	8.0	12.0
1322	1.0	2.0	4.0	8.0	12.0
1303	0.5	1.0	1.5	2.0	2.5

Standard vial 1303 contains acrolein and acrylonitrile. Due to the water soluble nature of these compounds the concentration levels in the standard are 25, 50, 75, 100 and 125 ug/l respectively.

Standard Analysis:

Immediately after the standards are prepared they are injected via the Teflon stopcock on the liquid sampling device (either a Tekmar LSC xxx or an OI xxx). The syringe containing the standards is injected first and then the syringe containing the 10 ml of water injected to give a final purge volume of 20 ml. The standard is purged eleven (11) minutes. Using the acquisition procedure AC the OWA prompts the operator for the sample description, the instrument number, the operator id number and any sample comments. The sample CompuChem number, EPA (or client) case number, EPA (or client) sample ID number and instrument number are entered into the sample description field. The other fields are filled out as required. After the sample purge is completed and the GC is ready the sampling device is set to desorb, automatically starting the GC/MS acquisition.

Quantitation:

Standards are quantitated using the OWA procedure RK invoking option 2. The proper syntax is:

RK <filename>#2,linkername

where linkername is WLDL. All required analytes (see attachment I) for this analysis must be found in each standard level. In the event that (a) compound(s) is (are) not detected by the RK procedure (due to a change in retention time(s) the quantitation list must be manually corrected and the corrected quantitation reprinted including the F2 (response factor) table. After creating a correct quantitation report, an updated 11-table must be created in order to properly quantitate any further standards, blanks or samples on that tune.

Generating the Initial Calibration:

After all five standards are acquired and processed the Initial Calibration is generated using the EPAMP procedure. The syntax for EPAMP is:

EPAMP linkername

where the linkername is WMDL. The program will prompt for the low, medium low, medium, medium high and high standard file names and generate a report listing all response factors, average response factors and percent relative standard deviation for each compound in tabular form. The operator is required to examine this report taking special care to note any compound with an excessively high percent RSD. If any corrections are made to any standard the EPAMP procedure must be repeated. All compounds labeled as CCC or SPCC must pass with

the exception that the SPCC criteria for 1,1,2,2- tetrachloroethane and bromoform are waived for this analysis. If the criteria for SPCC and CCC compounds are not met, the individual standards will be reanalyzed or the instrument will be re-evaluated and repaired. The tune will then be performed again. All Initial Calibrations must be reviewed and approved by a Senior GC/MS operator or a Data Review Specialist.

Definition of a Valid Initial Calibration:

1. One valid injection for each of five standard concentrations.
2. All standards acquired under a single valid tune.
3. All compounds present in all five (5) standards.
4. All CCC criteria met.
5. All SPCC criteria met.
6. Initial Calibration reviewed and signed by a Senior Operator or Data review Specialist.

SPCC Criteria:

The following compounds must have an average response factor greater than 0.300 in the Initial Calibration.

Chloromethane
1,1-Dichloroethane
Chlorobenzene

CCC Criteria:

The following compounds must have a percent relative standard deviation (%RSD) of less than or equal to 30 in the Initial Calibration.

Vinyl Chloride
1,1-Dichloroethene
Chloroform
1,2-Dichloropropane
Toluene
Ethylbenzene

Contents of the Initial Calibration Package:

A complete Initial Calibration package must contain all the following:

1. BFB tuning and mass calibration forms
2. A quantitation report for each standard
3. A labeled RIC for each standard
4. The Initial Calibration form generated by the EPAMP procedure

Continuing Calibration Standard

Frequency:

A Continuing Calibration Standard should be run immediately after the BFB analysis defining the start of a valid tune. A valid Continuing Calibration Standard must be obtained prior to the analysis of samples.

Nominal Concentration:

20 ug/l

No substitution of standard level is allowed.

Continuing Calibration Standard Preparation and analysis:

The calibration check standard is prepared exactly as the 20 ug/l Initial Calibration standard. See above for details.

Continuing Calibration Standard Requirements:

The Continuing Calibration Standard must meet prescribed requirements for SPCC and CCC compounds. If the SPCC and CCC criteria are not met, the standard will be reanalyzed or the instrument re-evaluated and repaired. The tune will then be performed again. The procedure EPAUP prints a report clearly noting whether all SPCC and CCC criteria are passed as well as updating the response factors in the libraries and the retention times in the 11-table for sample analysis. For this analysis (code 410) the SPCC criteria for bromoform and 1,1,2,2 tetrachloroethane are waived. All SPCC compounds must have a response factor greater than 0.300 and the response factor for all CCC compounds must be within 25 percent of the average response factor in the Initial Calibration. See above for a list of all SPCC and CCC compounds.

Contents of the Standard Package:

The complete standard package must contain the following:

1. BFB tuning and mass calibration forms.
2. A quantitation report form for the Continuing Calibration Standard.
3. A labeled RIC for the Continuing Calibration Standard.
4. A quantitation report for a valid blank.
5. The Continuing Calibration Standard form produced by EPAUP.
6. A labeled RIC for the instrument blank.
7. A compound list for the instrument blank which provides surrogate information.
8. Internal standard area monitor for the blank.
9. Spectra for any hits in the blank.
10. NBS library searches for any extraneous peaks in the blank.

Instrument Blank

Frequency:

A valid instrument blank must be obtained after a valid tune is established with both BFB and a valid shift standard and prior to the analysis of samples.

Instrument Blank Preparation:

An instrument blank is prepared by adding 8 ul of internal standard (ID#036) and 8 ul of surrogate standard (ID#392) to a 10 ml gas tight syringe containing 10 ml of sparged distilled deionized water. A second 10 ml syringe containing water from the same source is prepared concurrently. The syringe containing the internal standards and surrogates is injected through the Teflon stopcock into the purge vessel on the liquid sampling device. The syringe containing plain water is injected immediately after the syringe containing the internal standards and surrogates. The blank is treated for all purposes as a sample after this point. (See sample section for quantitation and work-up procedures).

Definition of a valid instrument blank:

A valid instrument blank must be obtained prior to the analysis of any samples. All compounds except for the common laboratory contaminants (defined in the Statement of Work as methylene chloride, acetone, toluene and 2-butanone) must not be present at concentrations above the method detection limit. Contractually, common laboratory contaminants may be present at up to 5 times the method detection limit. CompuChem has found that under normal circumstances toluene and 2-butanone should not be present above the method detection limit. In addition the CompuChem requirements for methylene chloride and acetone are as follows: If the first blank contains methylene chloride and acetone at greater than the detection limit run a second instrument blank. If the second blank contains methylene chloride and acetone at up to two (2) times the method detection limit and agrees closely with the first blank samples may be analyzed. Under unusual conditions the supervisor or their designee may allow concentrations of the common laboratory contaminants in the blank up to contractually allowed limits.

Sample Preparation

Sample Preparation:

Samples are provided to the laboratory in 40 ml vials with screw cap Teflon lined septa. Samples are prepared by gently pouring ten (10) mls of the sample into two separate 10 ml gas tight syringes from the 40 ml screw top vial. Internal standards (standard ID# 036) and surrogates (standard ID#394) are added to one of the ten (10) ml syringes. Matrix spikes are prepared as regular samples and ten (10) ul of the matrix spike standard (standard ID# 1001) are added. As defined in the statement of work the matrix spike contains 1,1-Dichloroethene, Trichloroethene, Benzene, Toluene and Chlorobenzene.

Sample Analysis:

Immediately after the sample is prepared, it is injected via a teflon stopcock into the purge vessel on the liquid sampling device and purged for eleven (11) minutes. During the purge time an acquisition is set up on the OWA using the procedure AC. The AC procedure prompts the user for sample, instrument number, operator number, and any relevant comments about the sample. At the Sample: prompt the operator enters the samples CompuChem number, the EPA case number, the EPA sample ID number, the instrument ID number and in the case of a sample spike the original CompuChem number. At the end of the purge time the liquid sampler is set to desorb and the acquisition is started on the OWA.

Quantitation:

The sample is quantitated using the automatic quantitation routine RK with the quantitation option two (2). This procedure produces a quantitation report with any found analyte values calculated against the response factor in the user libraries that was determined from the continuing calibration standard. This procedure also generates an RIC with the peaks corresponding to the internal standards and surrogates labeled with IS#x and S#x where x is the internal standard or surrogate number.

Generation of the Compound List:

The compound list is generated by the procedure CLISTE. The CLISTE procedure prompts the user for the sample analysis code and the volume of sample purged and produces a report containing reportable values for any analytes present, detection limits, surrogate recoveries and reports if the surrogate recoveries are in the appropriate range. This procedure also generates scan and library lists for any analytes present.

Generation of Spectra:

The statement of work for this analysis requires that both raw and background subtracted (enhanced) spectra and a comparison of the enhanced spectrum with an authentic instrument generated library spectrum be generated for each analyte found by the quantitation report. The procedure QLLGV does this automatically. The procedure should be executed immediately after the completion of the CLISTE procedure.

Library Searches:

The statement of Work for this analysis requires that all unidentified peaks in the RIC that are greater than ten (10) percent of the nearest internal standard (up to a maximum of ten (10)) be searched against the NBS library. This task is accomplished using the procedure UNKIDL. This procedure prompts the user for the EPA sample ID number, the EPA sample case number, the first scan of interest, and a sample correction factor. The procedure determines the peak(s) to be searched, generates the proper searches, calculates an estimated concentration for each peak, and prints a report containing the search results and estimated concentrations.

It is the responsibility of the operator to evaluate the library searches to determine if any target analytes were found but were not present in the quantitation report.

ATTACHMENT 1

(ALL UNITS ARE MICROGRAMS/LITER)

ANALYTE	CAS #	QUANTITATION LIMIT
Benezene	71-43-2	
Bromodichloromethane	75-27-4	1.5
Bromoform	75-25-2	1.5
Bromomethane	74-83-9	1.5
Carbon Tetrachloride	56-23-5	1.5
Chlorobenzene	108-30-7	1.5
Chloroethane	75-00-3	1.5
Chloroform	67-66-3	1.5
Chloromethane	74-87-3	1.5
Dibromochloromethane	124-48-1	1.5
1,1-Dichloroethane	75-34-3	1.5
1,2-Dichloroethane	107-06-2	1.5
1,1-Dichloroethene	75-35-4	1.5
Total -1,2-Dichloroethene		1.5
1,2-Dichloropropane	78-87-5	1.5
cis-1,3-Dichloropropene	10061-01-5	2.0
trans-1,3-Dichloropropene	10061-02-6	1.0
Ethyl Benzene	100-41-4	1.5
Methylene Chloride (*)	75-09-2	1.0
1,1,2,2-Tetrachloroethane	79-34-5	1.5
Tetrachloroethene	127-18-4	1.5
Toluene (*)	108-88-3	1.5
1,1,1-Tetrachloroethane	71-55-6	1.5
1,1,2-Tetrachloroethane	79-00-5	1.5
Trichloroethene	70-01-6	1.5
Vinyl Chloride	75-01-4	1.5
Acrolein	107-02-8	25
Acetone (*)	67-64-1	5.0
Acrylonitrile	107-13-1	25
Carbon Disulfide	75-15-0	3.0
2-Butanone (*)	78-93-3	5.0
Vinyl Acetate	108-05-4	5.0
4-Methyl-2-Pentanone	108-10-1	1.5
2-Hexanone	519-78-6	5.0
Styrene	100-42-5	1.0
m-Xylene **	108-38-3	1.5
o-Xylene **	95-47-6	1.5
p-Xylene **	106-42-3	1.5

* Common Laboratory Solvent

Blank Limit is 5x Method Detection Limit

** the m-Xylene, o-Xylene and p-Xylene are reported as a total of the three.

Documentation Form For:

Revising or Creating Standard Operating Procedures (SOPs): Including Designated Personnel Responsibilities

Revised Procedure ☒ New Procedure ☒ Procedure Attached

Instrument Procedure 410 : EPA LDL Water, Volatile 10-1-88
Procedure Area, Title, and SOP Number Effective Date

[Signature] 7/10/89
Procedure Prepared By Date

Susan W. Bass 2/14/89
Procedure Read, Understood, and Approved By Date
Appropriate Laboratory Station Manager

[Signature] 10/23/89
Procedure Read, Understood, and Approved By Date
Quality Assurance Representative

This procedure(s) meets the requirements as set forth in the following
References for Approved Methods:

USEPA Contract Laboratory Program, Statement of Work
for Organics Analysis, Multi-Media, Multi-Concentration,
2/88 - Region 5 SAS

These procedures describe how tasks are performed in this specific area.
If a question arises concerning the proper procedure to follow for an activity
in this area, these SOPs should be consulted to resolve the question. Also,
these SOPs are a valuable source of material for training purposes.

After the manager of this area believes the person responsible for these
tasks has mastered these SOPs, both the manager and the employee should sign and
date this form, assuring that these SOPs are understood and will be followed in
the daily operations of CompuChem Laboratories. Please forward a copy of this
revised or created SOP and a completed form to Quality Assurance.

Employee's name: _____ Date: _____

Employee's title: _____

Employee's name: _____ Date: _____

Employee's title: _____

Manager's name: _____ Date: _____

Manager's title: _____

Sample Preparation Procedure 3.2.1.6: (-89) Semi-Volatile Water Lower Detection Limit (LDL)

1.0 Summary of Method

A measured volume of water, approximately one liter, is solvent extracted with methylene chloride at a pH of greater than 11 and again at a pH of less than 2, using a separatory funnel or a continuous extractor. The separate extracts are dried and concentrated to 0.5 ml.

2.0 Reagents Used

2.1 50% Sodium Hydroxide - Only the extracted solutions may be used.

2.2 50% Sulfuric Acid - Only the extracted solutions may be used.

2.3 Methylene Chloride - A 60 ml tipet dispenser filled with pesticide grade methylene chloride is located at the low level liquid SV station. When refilling the tipet, do not lay the dispenser top on the counter, doing so may contaminate the tipet and subsequent samples.

2.4 Sodium Sulfate - Use only sodium sulfate labeled "FURNACED SODIUM SULFATE".

3.0 Surrogate and Spikes

3.1 Surrogate #393 add 100 ul to each sample and sample spikes.
B/N spike #2021 add 100 ul to each sample spike and blank spike.
Acid spike #3012 add 100 ul to each sample spike and blank spike.

4.0 Preparation of Equipment

4.1 Cover all work area with plastic-backed, absorbent table covering, with the plastic side down.

4.2 Assemble the following for each sample to be processed:

- a. One 2-liter separatory funnel with a ground-glass stopper and stopcock.
- b. Two 250 ml Erlenmeyer flasks.
- c. Two drying columns.
- d. Two K-D apparatus (consists of a concentrator tube and a K-D flask).
Only one is needed immediately. The second can be prepared after sample processing has been started.

- e. One glass stirring rod (can be used for all samples).
- f. Two 3-ball Snyder columns.

- 4.3 Rinse each of the items listed above (except the drying column) with methylene chloride (use the Teflon squeeze bottles). Empty the methylene chloride into a waste container. This practice is intended to prevent sample contamination. Please adhere to this practice. If the glassware selected for use is wet, it must be rinsed with acetone prior to the methylene chloride rinses. Several additional methylene chloride rinses should be performed to remove all possible contaminants contained in the acetone.
- 4.4 Add a small plug of glass wool to each drying column, then add 1-2 inches of prepared sodium sulfate to each drying column. Rinse the sodium sulfate with approximately 20 ml of methylene chloride for each rinse. Allow the methylene chloride to drain through the column into a waste container.
- 4.5 Place the 2-liter, separatory funnel in the rings located on one side of the rack, and place the Erlenmeyer flask on the counter top under each funnel. Place the drying column and K-D apparatus in the clamp on the other side of the rack, such that the tip of each prepared drying column is inside the neck of a K-D flask.

5.0 Other Materials Needed

- 5.1 Boiling Chips (Carborundum chips that have been soxhlet extracted with methylene chloride)
- 5.2 Rubber Bands
- 5.3 Nitrogen evaporation device
- 5.4 One 1-liter bottle
- 5.5 pH paper
- 5.6 Glass wool
- 5.7 Micropipet (100 ul capacity)

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Date: October 28, 1988
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5.8 Two 2 ml vials with Teflon-lined screw caps

6.0 Sample Preparation and Extraction

- 6.1 Use 1-liter of raw sample. Place it on the counter in front of the associated separatory funnels. Mark the level of the liquid on the bottle if the volume is less than a liter of sample, as this will allow measurement of the initial volume later. If any samples are contained in gallon or half-gallon bottles, prepare a liter bottle or liter graduated cylinder for measuring by rinsing with methylene chloride. Fill a liter bottle with sample from the gallon or half-gallon bottle. Pour the sample into the associated separatory funnels. Save the sample bottles and return to sample custodian.
- 6.2 Using a micropipet, add 100 μ l of surrogate standard #393 to each sample. It is important to add exactly 100 μ l to the entire liter of sample, including the sample spikes. Surrogate recoveries are used to judge the efficiency of the extraction. Record the surrogate ID number, lot number, and volume added, on the Extractions' Worksheet.
- 6.3 Add 100 μ l each of acid spike #3012 and base-neutral spike #2021 to any sample spikes or blank spikes included in the batch. Record the standard ID numbers, lot numbers, and volume added, on the Extractions' Worksheet.
- 6.4 Measure the initial pH, using wide-range pH paper.
- 6.5 Add 5 ml of 50% sodium hydroxide. Stopper the separatory funnel and shake for 20-30 seconds, venting the stopcock several times. Check the pH. If the value is 11 or greater, note the pH on the extraction worksheet. If the pH is not 11 or greater, continue to add 1 ml at a time of base, and shake until the pH has reached a value of 11 or greater. The sample is now ready for the base-neutral extraction.
- 6.6 Add 60 ml methylene chloride to each raw sample bottle or sample container. Rotate the containers to rinse all surfaces with the solvent and pour the methylene chloride into the appropriate 2-liter separatory funnel. Stopper each funnel and shake vigorously for 2 minutes. Be careful to vent the stopcock frequently, until the pressure equalizes.
- 6.7 Allow each separatory funnel to hang undisturbed for approximately 10 minutes, to allow the layers to separate. If an emulsion larger than two thirds the size of the bottom layer (methylene chloride) forms, steps must be taken to break it up. Emulsions may be broken by stirring, passing through the stopcock very slowly, or centrifugation. The method used is determined by the severity of the emulsion.

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- 6.8 When two distinct layers are obtained, drain the lower layer (methylene chloride) into the Erlenmeyer flask. Close the stopcock when the water layer reaches the stopcock. The object is to collect all the methylene chloride and none of the water.
- 6.9 Repeat Steps 6 thru 8 two more times, adding the methylene chloride directly to the separatory funnel.
- 6.10 Upon completion of the third extraction, pour the total extract through the drying column into the K-D apparatus. Rinse the Erlenmeyer flask with a small amount of methylene chloride and add the rinse to the drying column. Rinse the drying column with approximately 20 ml of methylene chloride and collect the rinse in the K-D apparatus.

NOTE: If recovery of the methylene chloride phase is less than 80%, see Sample Problem Techniques. (SPL #1.9.)

- 6.11 Remove the K-D apparatus containing the base-neutral extract. Replace it with the K-D set prepared for the acid extract and a new drying column containing sodium sulfate. The base-neutral extract is now ready for concentration. (See Extract Concentration Section F, below.)
- 6.12 Slowly add 10 ml of 50% sulfuric acid to each separatory funnel. Stopper the separatory funnel and shake 20-30 seconds, venting the stopcock several times. Check the pH. If the value is now 2 or less, note the pH on the Extractions' Worksheet. If the pH is not 2, continue to add 10 ml volumes of acid. Shake and measure the pH until a value of 2 or less is reached.
- 6.13 Once a pH of 2 or less has been reached, the sample is ready for the acid extraction. Perform Steps 6 thru 10, then Step 11.
- 6.14 Fill all sample bottles to mark with tap water. Use a 1000 ml graduated cylinder to measure the volume, and record the initial volume on the Extractions' Worksheet.

7.0 Extract Concentration

- 7.1. Add 1 or more boiling chips to each K-D flask and attach a Snyder column. Add 1-2 ml methylene chloride to the top of the Snyder column.
- 7.2. Place the K-D apparatus on a water bath set at 85°C or warmer to allow for a 10-15 minute concentration process.

7.3 Each K-D flask is removed from the bath as soon as an apparent volume of 4 ml is reached. Remove from bath and allow to drain. Remove the Snyder column and K-D flask from the concentrator tube, rinsing the tip of the K-D flask with a minimal amount of methylene chloride and remember to label the concentrator tubes with the proper label.

7.4 Nitrogen blowdown technique - Place the concentrator tube in a warm water bath (35°C) and evaporate the solvent volume to 0.5 ml using a gentle stream of clean, dry nitrogen (filtered through a column of activated carbon). The internal wall of the tube must be rinsed down several times with hexane during the operation and the final volume brought to 0.5 ml. During evaporation the extract must never be allowed to become dry.

7.5 Final concentration volume should be 0.5 ml.

NOTE: If sample cannot be concentrated down to 0.5 ml, see section on final volume.

7.6 Transfer the entire extract volume to a clear, 2 ml autosampler vial. Label the vial appropriately to indicate fraction type (blue to indicate base-neutral fraction and yellow to indicate acid fraction), prep code, CompuChem number, and completion date. At the time of transfer, note the final volume on the Extractions' Worksheet.

7.7 Complete paperwork and mark volume on vials and forward both to the person responsible for checking in paperwork.

7.8 Place paperwork and extracts in turn-in box.

8.0 Cleanup

8.1 Remove all of the water from each separatory funnel and place it in a labeled water-waste container.

8.2 Pour all waste solvent into the appropriate container.

8.3 Roll up all absorbent counter covers and place them in the trash can. Return any remaining sample and empty sample bottles to the sample cart.

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Revision No. 4
Date: July 1, 1989
Page 2 of 2

Documentation Form For:

Revising or Creating Standard Operating Procedures (SOPs): Including Designated Personnel Responsibilities

 Revised Procedure ✓ New Procedure ✓ Procedure Attached

SPP - 89: LDL Semivolatile / Water 10-28-88
Procedure Area, Title, and SOP Number Effective Date

[Signature] 10/28/88
Procedure Prepared By Date

[Signature] 10/28/88
Procedure Read, Understood, and Approved By Date
Appropriate Laboratory Station Manager

[Signature] 10/28/89
Procedure Read, Understood, and Approved By Date
Quality Assurance Representative

This procedure(s) meets the requirements as set forth in the following
References for Approved Methods:

F: USEPA Contract Laboratory Program, Statement of Work
for Organics Analysis, Multi-Media, Multi-Concentration,
2/88. Region 5 SAS

These procedures describe how tasks are performed in this specific area.
If a question arises concerning the proper procedure to follow for an activity
in this area, these SOPs should be consulted to resolve the question. Also,
these SOPs are a valuable source of material for training purposes.

After the manager of this area believes the person responsible for these
tasks has mastered these SOPs, both the manager and the employee should sign and
date this form, assuring that these SOPs are understood and will be followed in
the daily operations of CompuChem Laboratories. Please forward a copy of this
revised or created SOP and a completed form to Quality Assurance.

Employee's name: _____ Date: _____

Employee's title: _____

Employee's name: _____ Date: _____

Employee's title: _____

Manager's name: _____ Date: _____

Manager's title: _____

Identification #: 2393, 2394, 2395, 2396, 2397
Frequency of Analysis: Every twelve (12) hours

Section No. 4.2.15
Revision No. 0
Date: October 28, 1988
Page 2 of 3

SAMPLE IDENTIFICATION

Preparation Code: -89
Internal Standard ID: 035
Label: Prep Code, Date Blue
Yellow, Prep Code, Date

Surrogate ID#: 393
Vial Size: 2.0 ml
Storage: 40C

INJECTION PROCEDURE

4 inch needle Hamilton 10 ul syringe. 1.0 ul + 0.5 ul methylene chloride wash. "Cold Needle".

CHROMATOGRAPHIC MAINTENANCE

Benzidine response factor of .05 or greater.
PCP response factor of .05. or greater.

MISCELLANEOUS

Quantification Method: Library Entry
Quantification Method Name: SEMIL
Worksheet: Semiwork1, Semiwork2, Semiwork3
Compound List: 491
Library Names: R1-R7
File Naming Conventions: XX123456X78 Instrument #

ANALYSIS TYPE

Shift

Date/sample
EPA #, Case #

Analysis Type Prefixes

Calibration File: DH
Standard: HG
Initial Sample Injection: GH
Sample ReInjection: GJ
Sample Reextraction: GR
Sample Dilution: GD

Sample Preparation Procedure 3.2.2.14: (- 090) Lower Detection Limit (LDL)
Protocols for Water; Sample
Preparation for Pesticides/PCBs

1.0 Summary of Method

A measured volume of sample, approximately one liter, is solvent extracted with methylene chloride using a separatory funnel or a continuous extractor. The methylene chloride extract is dried, exchanged to hexane, and adjusted to a final volume of 5.0 ml. Optional cleanup techniques are included.

2.0 Interferences

- 2.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts and/or elevated baselines in gas chromatograms. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory reagent blanks. Interferences by phthalate esters can pose a major problem in pesticide analysis when using the electron capture detector. These compounds generally appear in the chromatogram as broad eluting peaks. Common flexible plastics contain varying amounts of phthalates. These phthalates are easily extracted or leached from such materials during laboratory operations. Cross-contamination of clean glassware routinely occurs when plastics are handled. Interferences from phthalates can best be minimized by avoiding the use of plastics in the laboratory. Exhaustive cleanup of reagents and glassware may be required to eliminate background phthalate contamination.
- 2.2 Matrix interferences may be caused by contaminants that are coextracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature and diversity of the site being sampled. The alumina column cleanup procedures must be used to overcome such interferences to attempt to achieve the MDLs.

3.0 Apparatus and Materials

3.1 Glassware

3.1.1 Separatory funnel - 2000 ml with Teflon stopcock.

3.1.2 Drying column - Chromatographic column approximately 400 mm long x 19 mm ID, with coarse frit. (Substitution of a small pad of disposable Pyrex glass wool for the frit will help prevent cross-contamination of sample extracts.)

- 3.1.3 Concentrator tube - Kuderna-Danish, 10 ml, graduated (Kontes K-570050-1025 or equivalent). Ground glass stopper may be used to prevent evaporation of extracts.
- 3.1.4 Evaporative flask - Kuderna-Danish, 500 ml (Kontes K-5700010500 or equivalent). Attach to concentrator tube with springs or rubber bands.
- 3.1.5 Snyder column - Kuderna-Danish, Three-ball macro (Kontes K-503000-0121 or equivalent).
- 3.1.6 Continuous liquid-liquid extractors - Equipped with Teflon or glass connecting joints and stopcocks requiring no lubrication. (Hershberg-Wolf Extractor-Ace Glass Company, Vineland, NJ P/N 6841-10 or equivalent).
- 3.1.7 Vials-Amber glass 1 to 2 ml capacity, with Teflon-lined screw cap.
- 3.1.8 Chromatographic column for alumina - 8 ml (200 mm x 8 mm ID) Polypropylene column (Kontes K-420160 or equivalent) or 6 ml (150 mm x 8 mm ID) glass column (Kontes K-420155 or equivalent), or 5 ml serological pipets plugged with a small piece of Pyrex glass wool in the tip. The Kontes columns may be plugged with Pyrex glass wool or a polyethylene porous disk (Kontes K-420162).
- 3.2 Pyrex glass wool - pre-rinse glass wool with appropriate solvents to ensure its cleanliness.
- 3.3 Silicon carbide boiling chips - Approximately 10/40 mesh. Heat to 400°C for 30 minutes or Soxhlet extract with methylene chloride.
- 3.4 Water bath - Heated with concentric ring cover, capable of temperature control ($\pm 2^{\circ}\text{C}$). The bath should be used in a hood.
- 3.5 Nitrogen evaporation device equipped with a water bath that can be maintained at 35-40°C. The N-Evap by Organomation Associates, Inc. South Berlin, MA (or equivalent) is suitable.
- 4.0 Reagents
 - 4.1 Reagent water - Reagent water is defined as a water in which an interferent is not observed at the MDL of each parameter of interest. Reagent water should be pre-extracted with methylene chloride. Using a 6 liter flask add 60 ml methylene chloride to deionized water and place a stir bar into flask and place on stirrer. Allow deionized water to extract for approximately 20 minutes.

- 4.2 Acetone, hexane, methylene chloride - Pesticide quality or equivalent.
- 4.3 Sodium sulfate - (ACS) granular, anhydrous. Purify by heating at 400°C for 4 hours in a shallow tray.
- 4.4 Alumina - Neutral, Super I Woelm or equivalent. Prepare activity III by adding 7% (v/w) reagent water to the Super I neutral alumina. Tumble or shake in a wrist action shaker for a minimum of 2 hours or preferably overnight. There should be no lumps present. Store in a tightly sealed glass container.
- 4.5 Sodium hydroxide solution (10N)-(ACS). Dissolve 40g NaOH in reagent water and dilute to 100 ml.
- 4.6 Sulfuric acid solution (1+1)-(ACS). Slowly, add 50 ml H₂SO₄ (sp. gr. 1.84) to 50 ml of reagent water.
- 4.7 Pesticide/PCB surrogate standard spiking solution. Solution #395
- 4.7.1 The compound specified is dibutyl chlorendate. The solution is at a concentration of 1 ug/1.0 ml in methanol.
- 4.8 Pesticide/PCB Matrix Standard Spiking Solution.
- 4.8.1 The spiking solution in methanol contains the following pesticides in the concentrations specified.

Pesticide	ug/1.0 ml
lindane	2.0
heptachlor	2.0
aldrin	2.0
dieldrin	5.0
endrin	5.0
4,4'DDT	5.0

- 4.9 Sample Extraction - Separatory Funnel.
- 5.0 Using a 1-liter graduated cylinder, measure out a 1-liter sample aliquot and place it into a 2-liter separatory funnel. Pipette 0.5 mL #395 surrogate standard spiking solution into the separatory funnel and mix well. Check the pH of the sample with wide range pH paper and adjust to between 5 and 9 pH with 10N sodium hydroxide and/or 1:1 sulfuric acid solution.

Note: Recovery of dibutylchloroendate will be low if pH is outside this range.

- 5.1 For duplicate sample spikes follow 5.0 using one original sample. Add 50 μ l of #4016 Pesticide Spiking Solution. Use 1000 ml sample volume for each duplicate sample spike.
- 5.2 Add 60 ml methylene chloride to the separatory funnel and extract the sample by shaking the funnel for two minutes with periodic venting to release excess pressure. Allow the organic layer to separate from the water phase for a minimum of 10 minutes. If the emulsion interface between layers is more than one-third the volume of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, and may include: stirring, filtration of the emulsion through glass wool, centrifugation, or other physical means. Drain methylene chloride into a 250 ml Erlenmeyer flask.
- 5.3 Add a second 60 ml volume methylene chloride to the sample bottle and repeat the extraction procedure a second time, combining the extracts in the Erlenmeyer flask. Perform a third extraction in the same manner.
- 5.4 Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10 ml concentrator tube to a 500 ml evaporative flask.
- 5.5 Pour the combined extract through a drying column containing about 10 cm of anhydrous sodium sulfate, and collect the extract in the K-D concentrator. Rinse the Erlenmeyer flask and column with 20 to 30 ml of methylene chloride to complete the quantitative transfer.
- 5.6 Add one or two clean boiling chips to the evaporative flask and attach a three-ball Snyder column. Pre-wet the Snyder column by adding about 1 ml methylene chloride to the top. Place the K-D apparatus on a hot water bath (80 to 90°C) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 10 to 15 minutes. At the proper rate of distillation, the balls of the column will actively chatter but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches 1 ml, remove the K-D apparatus. Allow it to drain and cool for it least 10 minutes.
- 5.7 Momentarily remove the Snyder column, add 60 ml of hexane and a new boiling chip and re-attach the Snyder column. Pre-wet the column by adding about 1 ml of hexane to the top. Concentrate the solvent extract as before. When the apparent volume of liquid reaches 1 ml, remove the K-D apparatus and allow it to drain and cool at least 10 minutes.
- 5.8 Remove the Snyder column, rinse the flask and its lower joint into the concentrator tube with 1 to 2 ml of hexane.

- 5.9 Nitrogen blowdown technique - Place the concentrator tube in a warm water bath (35°C) and evaporate the solvent volume to 0.5 ml using a gentle stream of clean, dry nitrogen (filtered through a column of activated carbon). The internal wall of the tube must be rinsed down several times with hexane during the operation and the final volume brought to 0.5 ml. During evaporation the extract must never be allowed to become dry.
- 5.10 Dilute the extract to 1 ml with acetone and proceed to the Alumina Column Cleanup.
- 6.0 Alumina Column Cleanup
- 6.1 Add 3 gm of activity III neutral alumina to the 10 ml chromatographic column. Tap the column to settle the alumina. Do not pre-wet the alumina.
- 6.2 Transfer the 1 ml of hexane/acetone extract to the top of the alumina using a disposable Pasteur pipet. Collect the eluate in a clean 10 ml concentrator tube.
- 6.3 Add 1 ml of hexane to the original extract concentrator tube to rinse it. Transfer the rinsing to the alumina column. Elute the column with an additional 9 ml of hexane. Do not allow the column to go dry during the addition and elution of the sample.
- 6.4 Concentrate the extract to a final volume of 5.0 ml using hexane. Transfer extract to amber, crimp-cap vials and along with accurately completed paper work, turn in to the GC lab for analysis.

Documentation Form For:

Revising or Creating Standard Operating Procedures (SOPs): Including Designated Personnel Responsibilities

Revised Procedure ☒ New Procedure ☒ Procedure Attached

SPP -90: L.D.L. Waters/ PEST. and PCBs
Procedure Area, Title, and SOP Number

10-28-88
Effective Date

[Signature]
Procedure Prepared By

10/28/88
Date

[Signature]
Procedure Read, Understood, and Approved By
Appropriate Laboratory Station Manager

10/28/88
Date

[Signature]
Procedure Read, Understood, and Approved By
Quality Assurance Representative

10/23/89
Date

This procedure(s) meets the requirements as set forth in the following
References for Approved Methods:

USEPA Contract Lab. Program, Statement of Work for Organic Analysis
Multi-Media, Multi-Concentration, 2/88. - Region 5 SAS

These procedures describe how tasks are performed in this specific area.
If a question arises concerning the proper procedure to follow for an activity
in this area, these SOPs should be consulted to resolve the question. Also,
these SOPs are a valuable source of material for training purposes.

After the manager of this area believes the person responsible for these
tasks has mastered these SOPs, both the manager and the employee should sign and
date this form, assuring that these SOPs are understood and will be followed in
the daily operations of CompuChem Laboratories. Please forward a copy of this
revised or created SOP and a completed form to Quality Assurance.

Employee's name: _____ Date: _____

Employee's title: _____

Employee's name: _____ Date: _____

Employee's title: _____

Manager's name: _____ Date: _____

Manager's title: _____

SAMPLES

Samples are provided to the laboratory in 40 ml vials with screw cap teflon-lined septa. Samples are prepared by gently pouring 25 mls of the sample into gas tight syringes from the 40 ml vial. To this volume of the sample, are injected 5 ul of Internal Standard #036 and 5 ul of Surrogate #394. Sample spikes and blank spikes also require the addition of 10 ul of #1001 which contains 1,1-Dichloroethylene, Trichloroethylene, Benzene, Toluene and Chlorobenzene.

SAMPLE ANALYSIS:

Immediately after the sample is prepared, it is injected via the teflon stopcock on the Tekmar into the purge vessel and purged for twelve (12) minutes. The sample is analyzed using the AC program in the form

AC filename # number of scans to acquire

Next enter the appropriate information for sample description, including instrument ID and the operator ID (as prompted by the program). When the information has been entered and the instrument is ready, the Tekmar is switched to the desorb position and the sample will be introduced onto the head of the column. The data acquisition will continue unsupervised until the designated number of scans has been acquired.

QUANTITATION:

The sample is quantitated using the RK program with option 2. The RK procedure allows individual compounds to be quantitated using the calibration check standard for the particular analysis. The RK procedure is initiated by typing the command in the form

RK filename #2, linker

using the linker appropriate for the type of analysis. If any internal standards, surrogates or other compounds are not found they can be found by using the UPQUAN program in the form

UPQUAN LIBRARY ID # LIBRARY ENTRY

for each compound not found. If any internal standard must be UPQUANed then all compounds which reference that internal standard must also be UPQUANed to insure that the amounts reported for those compounds will be accurate. If any compounds are UPQUANed the quantitation list must be sorted. This can be accomplished by using the EQL program in the form

EQL filename , filename

and deleting any duplicate entries as necessary. When the quantitation list has been edited, the quantitation list can be

sorted using the QSORT program in the form

QSORT filename , linker

using the linker appropriate for the type of analysis. The quantitation list can be reprinted using the MQ program in the form

MQ filename ;F2;H;E

which will print the compound list and the F2 table.

GENERATION OF THE COMPOUND LIST:

The compound list can be generated by using the CLISTE program in the form

CLISTE filename , linker

with the appropriate linker for the type of analysis. The program will prompt the operator to enter the appropriate compound list number and the volume of the sample purged.

GENERATION OF SPECTRA:

The dual spectra and comparative spectra of any compounds found can be generated by simply typing QLLGV.

LIBRARY SEARCHES:

If there are any peaks in the RIC that do not correspond to entries in the compound list and are greater than or equal to 10% of the height of the closest internal standard, then a library search must be performed. This is accomplished by the UNKIDL program in the form

UNKIDL filename , linker , \$ number of searches

using the appropriate linker and number of searched required by the analysis. The program will prompt the user for EPA number, the first scan of interest, the last scan of interest, and the correction factor (this can be found on the last page of the compound list). Library searches must be evaluated to see if any priority pollutants were found that are not present in the quantitation report.

EVALUATION OF DATA:

For blanks, samples, sample spikes, and blank spikes all surrogates must fall within the specified control limits. In addition, all internal standards must pass the criteria of the Internal Standard Area Monitor. Any samples that fail the above criteria must be reprepared and reinjected. If multiple samples fail these criteria the problem should be corrected before any further samples are analyzed. In addition, the quantitated values

for any compounds found in a diluted sample must fall within the range from 20 - 40 ug/l, or be analyzed again at a smaller dilution (or neat). Any sample with compounds outside this range that has not been analyzed using 25 ml must be diluted accordingly and reinjected.

Instrument Procedure: Lower Detection Limit; Water; Pesticide/PCB
Analysis (Res Well) Instrument Code No. 152

This analysis can be done on different packed or megabore capillary columns with two different instrument conditions. The sample must be run on one of the column types, and if pesticides or PCBs are indicated, confirmed on the other type of column.

Section I. Instrument Conditions

Analytical Column #1

3% OV-101 On 100/120 mesh Supelcoport 6'x2mm ID or megabore capillary column equivalent

Gas Chromatographic Conditions

Carrier Gas: Argon/Methan at 15 mls/min

Injection Port: Flash vaporizing at 220°C

Oven: Isothermal in the range 190-210°C. Adjusted so that retention time of PP'DDT is in the range of 11.5 to 12.5 min.

Detector: ECD at 300°C

Sample Injection

1.0ul by autosampler

Analytical Column #2

1.5% SP2250/1.95%SP2401 on 100/120 mesh Supelcoport 2m x 4mm ID or megabore capillary column equivalent

GAS Chromatographic Conditions

Carrier Gas: Argon/Methane at 60 mls/min

Injection Port: Flash vaporizing at 240°C

Oven: Isothermal in the range 210-230°C. Set so that retention time of PP'DDT is after 12.0 min.

Detector: ECD at 300°C

Sample Injection

5.0ul by autosampler

Section II. Standards, Surrogates, Spikes and Detection Levels

Standards

- 1) A three point linearity standard set is run every 72 hours
- 2) A full set of standards containing all the pesticides and Aroclors is run every 72 hours.
- 3) A column evaluation or response check standard is run after every five samples.
- 4) Both response check standards are run at the end of each sequence.

For every sequence, data is collected on the linearity of Aldrin, Endrin, PP-DDT and dibutylchlorodate; the percent breakdown of Endrin and PP'DDT, and the retention time shift of DBC throughout the run. This data is displayed on Form VIII and is calculated with the help of the computer program EPAEV. This program can be run by any properly trained analyst or technician.

The Pesticide/PCB library is generated for every sequence by the analysis of the retention times and areas of the peaks in the full set of standards. This analysis is done with the help of the computer program EPACK. In addition to generating a library, EPACK also calculates the percent difference of each of the check standards run during the course of the sequence. This program can be run by any properly trained technician or analyst.

Surrogates

Dibutylchloroendate

Recovery must be greater than 25% for acceptance

Spikes

The normal spiking solution contains the following compounds and must meet the following recovery criteria:

<u>Compound</u>	<u>Level</u>	<u>Recovery Range Water</u>
Gamma BHC	0.01 ug/ml	56 - 123
Heptachlor	0.01 ug/ml	40 - 131
Aldrin	0.01 ug/ml	40 - 120
Dieldrin	0.025 ug/ml	52 - 126
Endrin	0.025 ug/ml	56 - 121
PP' DDT	0.025 ug/ml	38 - 127

Sample spike recoveries may not be available due to dilution of the sample due to compounds in the matrix other than the spike (pesticide or non-pesticide). If recoveries are available, they must meet the current recovery and duplicate criteria. If sample spike recoveries are not available, blank spike data will be used to demonstrate extraction and analytical control.

Standard Levels

The normal standards contain the following pesticides and Aroclors at the following levels. The detection level for water is based on a sample amount of one liter and an extract amount of 5 mls. Any dilution or smaller sample amount will raise the detection level.

Table 1. Standard amounts and normal detection levels.

<u>Standard 4360</u>	<u>Level In Standards</u>	<u>CRQL</u>
<u>Compound</u>	<u>4360/4364</u>	<u>Water</u>
Gamma BHC	0.01 ug/ml	0.005
Heptachlor	0.01 ug/ml	0.005
Aldrin	0.01 ug/ml	0.005
Gamma Chlordane	0.01 ug/ml	0.05
Endosulfan I	0.01 ug/ml	0.01
Dieldrin	0.02 ug/ml	0.01
Endosulfan II	0.04 ug/ml	0.01
PP' DDT	0.06 ug/ml	0.01

<u>Standard 4360</u> <u>Compound</u>	<u>Level In Standards</u> <u>4360/4364</u>	<u>CRQL</u> <u>Water</u>
DBC (Surr)	0.10	
PP-Methoxychlor	0.05	0.05 -
Alpha BHC	0.01	0.005 -
Beta BHC	0.02	0.005
Delta BHC	0.01	0.005
Heptachlor Epoxide	0.01	0.005
Alpha Chlordane	0.02	0.05
PP-DDE	0.02	0.01
Endrin	0.04	0.01
PP-DDD	0.04	0.01
Endosulfan Sulfate	0.04	0.01
Endrin Ketones	0.10	0.01

Individual multi peak pesticides and Aroclor mixtures

Toxaphene	1.0	0.10
PCB 1221	1.0	0.05
PCB 1232	0.7	0.05
PCB 1016	0.3	0.05
PCB 1242	0.4	0.05
PCB 1248	0.4	0.05
PCB 1254	0.3	0.10
PCB 1260	0.3	0.10

Section III. Compound Identification

A compound is identified as being in a sample if that compound is found on two different types of columns. In order for a single component pesticide to be found in a run, its retention time must be within the retention time window of a pesticide of interest. The size of that window is either $\pm 2\%$ for packed or $\pm 1.5\%$ for wide bore capillary or smaller. A smaller window may be set if there are enough samples or standards run with detectable levels of DBC so that a retention time shift can be observed throughout the sequence. Once a compound is identified on one column, the sample is run on the other column.

Multi components pesticides and Aroclors are identified by pattern as well as retention time. The identification and quantitation of these compounds is very complex and many decisions are based on the experience of the analyst, however there are some tools and guidelines employed by the GC lab.

Guidelines

- 1) The sample should contain the three largest peaks in the aroclor and at least two other minor peaks.
- 2) The RSD of the pattern match (see tools below) should be less than 33%.
- 3) The compound with the best pattern match should be chosen.

- 4) If an identification is made even though one of the previous guidelines are not met, the analyst should provide notes on why he thought the compound was there.

Tools

Pattern recognition is done with the help of a computer program which compares the sample and the standards peak for peak, adds up the total number of common peaks found and calculates the area ratios of the common peaks. It then runs a standard deviation test on all the ratios, calculates the mean value and discards any peak ratio outside of a $\pm 2\sigma$ standard deviation window from the mean and recalculates the mean and standard deviation. This continues until no ratios are discarded during a pass or there are no ratios left. The values are printed out for every pass and the relative size of the standard deviation to the mean (RSD) is calculated. An example of the computer printout follows. This data may not be used if there are multiple Aroclors in the sample with common PCBs or the match is so good that the standard deviation is too small and valid data is discarded. In the first case, the analyst must proceed on his own and in the second case, the analyst may take calculated values from other than the last pass. In most cases the change in the mean from first to last pass is so small it is insignificant.

Section IV Compound Quantitation

If a compound is identified, it is quantitated using the following formula

$$\text{amount} = \frac{\text{area of sample/area of std} \times \text{conc of std} \times \text{dilution} \times \text{volume of extract}}{\text{Volume of sample}}$$

In case of multi component compounds, area of sample/area of standard is replaced with the mean ratio of all peaks used.

Example: One liter of a water sample is extracted with a final extraction volume of 10 mls. The extract is diluted 1:10 for analysis and Gamma BHC is identified and quantitated on a OV-101 column using the 4360 standard. The area of the sample peak was 437 and the area of the standard peak was 351. The calculation would be set up as follows:

$$\text{amount of Gamma BHC} = \frac{437/351 \times 0.01\mu\text{g/ml} \times 10 \times 10\text{mls}}{1.0 \text{ liters}} = 1.24\mu\text{g/l}$$

The actual calculation is usually made with the help of program EPACA. This program generates an Analysis Worksheet which shows all the data used in the generation of the results. It also generates a copy of the form ID and form 8.

Section V Quality Assurance/Quality Control

See QA/QC section for blank, spike and duplicate information.

In addition to the CompuChem QC samples, there are special GC lab QA measures. Each sample must pass the following criteria:

- 1) Complete injection was made
 - a) good surrogate recovery if surrogate is available

- b) reasonable solvent peak if surrogate is not available
 - 2) No carryover contamination
 - a) No late eluting peaks from previous injection
 - b) No syringe contamination from previous injection
 - 3) No retention time shift
 - a) Surrogate must be within window if available
 - b) Surrogate in standard before and after sample must be within window if surrogate not in sample.
- If one or more of these criteria are not met, the sample is reanalyzed.

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APPENDIX B-2
TOC ANALYSIS OF SOILS

**QUALITY CONTROL REQUIREMENTS FOR THE
ANALYSIS OF TOTAL ORGANIC CARBON BY RMT
FOR THE ACS SITE**

④ Provided in this appendix is the standard operating procedure for the analysis of Total Organic Carbon (TOC) on soil and sediment samples from the ACS Site. The following table lists frequency and performance standards for QC samples. If QC check samples do not meet performance standards, the samples are to be reanalyzed. If a duplicate or spike does not meet the specified limits, the sample will be reanalyzed immediately. If the re-analysis still does not meet the specified limits, the affected data will be flagged. When the concentration exceeds the calibration range, re-analysis of the prepared sample at the appropriate dilution is required.

<u>Parameter</u>	<u>Audit</u>	<u>Frequency*</u>	<u>Limits</u>
① Total Organic Carbon No Det Lim	Lab Blank	1 per 10 samples	<Detection Limit (DL)
	Check Standard	1 per 10 samples	90-110% Recovery
	EPA QC Reference Standard	1 per set	80-120% Recovery
	Lab Duplicate	1 per 10 samples	20 RPD (;DL if sample concentration is <5 x DL)
	Matrix Spike	1 per 10 samples	75-125% recovery

*Frequencies apply to each matrix individually.



Total Organic Carbon Analysis

APPLICATION: To analyze water and wastewater for nonpurgeable organic carbon.

REFERENCE: EPA Method 415.1, 1974
EPA SW846 Method 9060, September 1986
Standard methods 505, 1985
Dohrmann DC-80 TOC systems manual, ed. 6, January 1984

SAMPLE HANDLING & PRESERVATION:

(13) (7) put no size
The sample is preserved at the time of sampling by acidifying to pH ≤ 2 with H_2SO_4 . The sample is refrigerated in a glass bottle. Hold time for the preserved sample is 28 days.

INTERFERENCES:

(16)
The presence of chloride in high concentrations ($> 0.10X$) interferes with the rate of oxidation. The tailing which results may fall outside of the 8 minute analysis window. The reagent can be slightly modified by adding mercuric chloride and mercuric nitrate. The chloride then complexes with the mercury which in turn allows the carbon to oxidize at a normal rate. The procedure can be found on page 7-1 of the systems manual.

Highly suspended solids can also give variable results. However, it is imperative that the sample be suspended evenly if total organic carbon is being measured. Settling should not occur before injection. Particles may clog the autosampler tubing. Therefore, samples with suspended matter must be manually injected.

APPARATUS:

Dohrmann DC 80 Total Organic Carbon Analyzer
18 x 150 mm test tubes (to hold samples)
Syringes (1 ml, 100-250 ul, 50 ul)

REAGENTS:

(1) Reagent water: Deionized water

(2) Potassium Persulfate Solution, 2%:

(11)
Dissolve 20g potassium persulfate in 1000 ml d.i. water, add 1 ml concentrated Nitric Acid, mix well. Store in cool dark place.
Shelf life is one month.



LABORATORIES

(3) Potassium Persulfate - Mercuric Salt Solution:

Dissolve 8.2g HgCL and 9.6g Hg₂NO₃H₂O in 400 ml d.i. water, add 20g Potassium Persulfate and 5 ml concentrated Nitric Acid, mix well, bring to 1 L with d.i. water.

STANDARDS: (ppm as Carbon)

(11)

- (1) 2000 ppm: 425 mg reagent grade Potassium Hydrogen Phthalate, KHP, plus 0.1 ml concentrated HNO₃ in 100 ml d.i. water. Store in amber bottle, refrigerate. Shelf life is one month.
- (2) 400 ppm: Dilute 20.0 ml of 2000 ppm Standard to 100 ml in volumetric flask. Store in amber bottle, refrigerate. Shelf life is one week.
- (3) 10 ppm: Dilute 1.0 ml of 2000 ppm Standard to 200 ml in volumetric flask. Store in amber bottle, refrigerate. Shelf life is one week.

CALIBRATION:

(12)

The instrument is calibrated from a one point standard. When **CAL** light is off, the instrument has no calibration in its memory.

To calibrate:

- (1) inject standard
- (2) push **START**
- (3) when **READY** light comes on, push **CAL**. **CAL** light should now be on.

When **CAL** light is on, the instrument is already storing a calibration. In most cases an update of the existing calibration is sufficient. Follow the same calibration steps to update a calibration (the **CAL** light should remain on the entire time).

In order to erase an existing calibration from memory, simply hold **CAL** in for at least 1 second. The **CAL** light will go off.

RANGES:			Calibration with
			(2)
0.1 - 20 ppm	use 1000 ul injections	10 ppm KHP	
10 - 800 ppm	use 200 ul injections	400 ppm KHP	
100 - 4000 ppm	use 40 ul injections	2000 ppm KHP	

When selecting a range, make sure the selector knob on the front panel is in the correct position.

PROCEDURE:

1. Start up:

Three **POWER**'s are turned on - right to left. NOTE: main power (toggle switch) on the detector always remains on.
Gas supply is turned up to 30 psi oxygen.



Pump fingers are put in place.

PUMP is turned on.

LAMP should be on. (The door must be closed for the UV light to come on).

When the baseline is stabilized around 0.0100, the instrument is ready for the first injection.

2. Instrument is calibrated (see "Calibration")

3. Sample is prepared for injection:

Sample is shook vigorously and poured into labeled test tube.

(All sediment must be suspended evenly)

Sample is sparged for 10 minutes with oxygen.

Syringe is used to agitate the sample to insure uniform suspension of solids.

Syringe is filled to sample volume.

*No sample size.
But is it important?*

4. Sample is injected and **START** is pushed.

When the sample has been processed, the **READY** light will come on and the integrated concentration will be sent to the printer. This indicates that the instrument is ready for the next injection.

5. To shut the instrument down:

Three **POWER**'s are turned off - left to right.

Gas supply is turned off.

The reagent supply tube and two waste exit tubes are disconnected to prevent syphoning.

Pump fingers are released.

AUTOSAMPLER OPERATION:

The autosampler is loaded from the outside first with test tubes. Sample 1 is to the right of the grey tube plug. Samples 1-4 should be KHP standards - the first three to calibrate and the last for a check. Sample 5 should be a reference standard, and sample 6 should be a water blank.

The autosampler MUST be calibrated separately from the manual injection mode.

Make sure the sample loop size corresponds to the range selected.

Samples are loaded clockwise around the outside ring (samples 1-59). Sample position 60 is directly inside the grey tube plug. Samples 60-62 should be standards or blanks. The inside ring is also loaded clockwise.

To start the autosampler: Position tube 1 directly beneath sampling arm. (The sample tray must only be moved counter-clockwise). The two probes to the right of the sampling arm will sparge the sample. No pre-sparging is necessary. (Particles may clog the autosampler tubing. Therefore, samples with suspended matter must be manually injected).

Press **AUTO** and observe proper operation.

A small magnet provided may be used to stop the autosampler automatically. This is done by placing it on the tray two positions past the last sample.

**ERROR MESSAGES:**

ERROR will light up whenever an integration is not acceptable, or has been interrupted. For an explanation of the sources of possible error see pg. 3-10 of the manual.

The instrument is ready for the next injection when the **READY** light is on, even if the **ERROR** light is on.

QUALITY CONTROL:

(10)
A water blank and calibration standard are run each day to verify calibration. Recalibration (or updating an existing calibration) is necessary if standards vary by more than 10% from calibration. A check standard is run after every 10 samples to monitor system stability.

Duplicates are run for 10% of the samples.

Spikes (usually at 10 parts per million) are run at a frequency of 10% of samples. If recovery is out of range, the spike is repeated. If it is still out of range, a different sample is spiked. If new spike is in range, matrix interference of the first sample is indicated.

Reference standard is run each day.

Duplicate values are spike recovery are charted to monitor precision and accuracy over time.



Appendix

APPLICATION: To analyze soil, sludge, and solid waste for organic carbon.

REFERENCE: ASTM Method D4129-82, 1982.
Dohrmann DC-80 TOC Systems Manual, ed. 6, January 1984.

SAMPLE HANDLING AND PRESERVATION:

The sample is not preserved, but is refrigerated in a glass bottle.

APPARATUS:

Dohrmann DC 80 Total Organic Carbon Analyzer with Sludge and Sediment
Sample Accessory
Forceps
Watch Glass
50 uL Syringe
Small Spatula
Platinum Boat

PROCEDURE:

1. Start up:

Three POWER 's are turn on--right to left. Furnace is turned on. Gas supply is turned up to 30 psi oxygen. The furnace must be allowed to warm up for approximately one hour. During this time, the two tubes from the furnace should be immersed in water, pH = 10, to absorb any NO_x that may be formed. The furnace is ready when the tube near the sample inlet is glowing. When the baseline is stabilized around 0.0100, the instrument is ready for the first injection. The PUMP and LAMP do not have to be turned on.

The teflon loop is removed form inlets 4 and 5 on the reaction module and lines 4 and 5 from the furnace are attached in its place.

2. Boat preparation:

The platinum boat is lined with quartz wool. The boat is introduced into the furnace and allowed to "bake-out".

3. The instrument is calibrated using 2000 ppm KIIP standard. The standard is injected into the boat through a septa in the sample port.

4. Sample preparation:

Sample is mixed until homogeneous.

Transfer approximately 5 grams of sample into a porcelain dish. Add 5% sulfuric acid dropwise, while mixing, until effervescence is no longer visible. Dry in an oven at 105°C until constant dry weight is obtained.

(13) +

(9) Sample size

LABORATORIES

Sample is weight into a lined platinum boat. (Sample size must be kept between 10 and 100 mg.)

Sample is placed in the saddle and the injection port is closed. Sample is allowed to stand outside of furnace for about 2 minutes to stabilize the system.

Note: When calibrating, the boat is immediately introduced into the furnace.

- (14) If the machine is automatic DO we have to get an engineering schematic?
5. START is pushed and sample is introduced into the furnace. When the sample has been processed, the READY light will come on and the integrated concentration will be sent to the printer. This indicates that the instrument is ready for the next sample.
 6. Instrument shut down:

Three POWER 's are turned off--left to right. Gas supply is turned off. The reagent supply tube, the two waste exit tubes, and lines 4 and 5 are disconnected to prevent syphoning.

15 - NO flow chart
 16 -
 17 -
 18 -
 19 -
 20 -

16-20
 show us a typical
 RUN on the
 machine.



APPENDIX B-3
GROUNDWATER FIELD SCREENING METHOD



PREPARED FOR:

**Warzyn Engineering, Inc.
One Science Court
Madison, Wisconsin 53705**

**SOIL GAS SURVEY
FIELD OPERATION PLAN**

December 1989

SUBMITTED BY:

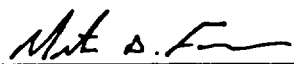

Tracer Research Corporation



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INTRODUCTION

This Field Operation Plan addresses Tracer Research Corporation's procedures for the collection and analysis of groundwater samples. The following list includes typical detection limits for some target volatile organic compounds (VOCs) in both soil gas and groundwater using direct injection techniques. These detection limits are based on maximum injection volumes of 2 mL of gas or 5 μ L of water.

COMPOUND	*SOIL GAS (μ g/L)	GROUNDWATER (μ g/L)
1,1-dichloroethene	0.05	1
1,1-dichloroethane	0.01	2
chloroform	0.001	0.5
carbon tetrachloride	0.00005	0.01
1,1,2-trichlorotrifluoroethane	0.0001	0.05
vinyl chloride	0.01	2
trans-1,2-trichloroethene	0.01	2
methylene chloride	0.01	2
1,1,1-trichloroethane	0.0001	0.02
trichloroethene	0.0001	0.02
benzene	0.02	4
toluene	0.02	4
xlenes	0.02	4
total petroleum hydrocarbons	0.02	4

The stated detection limits for water samples can be lowered by a factor of 10 to 100 by using headspace analysis techniques. The exact amount the detection limit can be lowered is dependant on the individual compound's partition coefficient.

GROUNDWATER SAMPLING PROCEDURES

Water samples are collected by driving hollow probes with detachable tips below the water table and then withdrawing the probes to permit water inflow into the resulting hole. A vacuum adaptor is placed on the top of the probe and is used to connect to the vacuum pump (Figure 1). A vacuum of up to 27 inches of mercury is applied to the interior of the probe and open hole until water is drawn up the probe. Normally, water can be sampled within 10 minutes. If the formation is unusually tight and does not yield water fast enough



to fill the pipe, a vacuum can be applied to the probe for an indefinite period. After remaining under vacuum for 15 to 20 minutes, usually some water is drawn into the open hole or up into the pipe. The water thus accumulated is then removed by drawing a vacuum on a 1/4 inch polyethylene tube inserted down the probe to the bottom of the open hole. After the tube fills with water it is removed and drained in to a 40 mL VOA bottle. This procedure allows a water sample to be collected in a short time from very tight formations that might otherwise require hours or days to collect by conventional means. Loss of volatile compounds by evaporation is accordingly reduced when water is induced to flow into the very narrow hole, because it can be sampled with little exposure to air or none at all if the sample is drained directly out of the probe and through the tubing. The polyethylene tubing is only used once and then discarded to avoid any cross-contamination problems.

Water samples are collected in 40 mL VOC vials that are filled to exclude any air and then capped with Teflon-lined septa caps. Water samples are permitted to stand up to several hours if necessary before chromatographic analysis in order to ensure that a sediment-free sample can be withdrawn from the top portion of the vial. Water samples are subsampled and analyzed by direct injection in volumes ranging from 0.2 uL to 5 uL, depending upon the contaminant concentrations.

Groundwater samples can also be analyzed by injecting headspace in the sample container created by decanting off approximately half of the liquid in the bottle. Headspace analysis is the preferred technique when a large number of water samples are to be performed daily. The method is more time efficient for the measurement of volatile organics than direct injection because there is less chance for semi-volatile and non-volatile organics to contaminate the system as there is with direct injection. Depending upon the partitioning coefficient of a given compound, the headspace analysis technique can also yield greater sensitivity than the direct injection technique.



ANALYTICAL PROCEDURES

I. Varian 3300 Gas Chromatograph

A) Equipped with Electron Capture Detectors (ECD), Flame Ionization Detectors (FID), Photo Ionization Detectors (PID) and/or Thermal Conductivity (TC) Detectors.

B) The chromatographic column used by TRC for the analysis of halocarbons is a 1/8" diameter packed column containing Alltech OV-101. This nicely separates most of the tri-chloro and tetra-chloro compounds that are encountered in soil gas investigations. The di-chloro compounds tend to elute ahead of the tri-chloro and tetra-chloro compounds, thus creating no interference. In the event that assurance of the identity of a compound in any particular sample is needed, it will be analyzed on a SP-1000 column after the OV-101 analysis.

II. Two Spectra Physics SP4270 Computing Integrators.

The integrators are used to plot the chromatogram and measure the size of the chromatographic peaks. The integrators compute and record the area of each peak. The peak areas are used directly in calculation of contaminant concentration.

III. Chemical Standards From ChemServices, Inc. of Westchester, Pennsylvania.

A) TRC uses analytical standards that are preanalyzed, of certified purities and lot numbered for quality control assurance. Each vial is marked with an expiration date. All analytical standards are the highest grade available. Certified purities are typically 99%.

B) The Quality Assurance procedures used by ChemService were described by the Laboratory Supervisor, Dr. Lyle Phipper:

- 1) The primary measurement equipment at ChemServices, the analytical balance, is serviced by the Mettler Balance Company



on an annual basis and recalibrated with NBS traceable weights.

2) All chemicals purchased for use in making the standards are checked for purity by means of gas chromatography using a thermal conductivity detector. Their chemicals are purified as needed.

3) The information on the purification and analysis of the standards is made available upon request for any item they ship when the item is identified by lot number. All standards and chemicals are shipped with their lot numbers printed on them. The standards used by TRC are made up in a two step dilution of the pure chemical furnished by ChemServices.

IV. Analytical Supplies

1. Sufficient 2 and 10 cc glass and Hamilton syringes so that none have to be reused without first being cleaned.
2. Disposable lab supplies, where appropriate.
3. Glassware to prepare aqueous standards.
4. Miscellaneous laboratory supplies.



QA/QC PROCEDURES

I. Standards

A) A fresh standard is prepared each day. The standards are made by serial dilution.

1) First, a stock solution containing the standard in methanol is prepared at TRC offices in Tucson. The stock solution is prepared by pipetting the pure chemical into 250 mL of methanol in a volumetric flask at room temperature. The absolute mass is determined from the product of volume and density calculated at room temperature. Hamilton microliter syringes, with a manufacturer's stated accuracy of + or - 1%, are used for pipetting. Information on density is obtained from the CRC Handbook of Physics and Chemistry. Once the stock solution is prepared, typically in concentration range of 50-1000 mg/L, a working standard is prepared in water each day. The solute in the stock solution has a strong affinity to remain in methanol so there is no need to refrigerate the stock solution. Additionally, the solute tends not to biodegrade or volatilize out of the stock solution.

2) The working standards are prepared in 40 mL VOA septum vials by diluting the appropriate ug/L quantity of the standard solution into 40 mL of water.

B) The standard water is analyzed for contamination before making the aqueous standard each day.

C) The aqueous standard is prepared in a clean vial using the same syringe each day. The syringe should only be used for that standard.

D) Final dilution of the calibration standards are made in water in a VOA vial having a Teflon coated septum cap instead of in a volumetric flask in



order to have the standard in a container with no air exposure. The VOA bottle permits mixing of the standard solution and subsequent syringe sampling all day long without opening the bottle or exposing it to air. The measurement uncertainty inherent in the use of a VOA bottle instead of a volumetric flask is approximately + or - 1%.

E) If headspace analyses are performed, a 3-point headspace calibration will be performed at the beginning of the day. The aqueous standards will contain the compounds of interest in the range of 5 to 1000 ug/L depending on the detectability of the individual components. Three check standards will be analyzed once at the beginning of the day to determine the mean response factor (RF) for each component (Figure 3). One of the three check standards will be injected again after every fifth sample to check detector response and chromatographic performance of the instrument throughout the day.

F) The RF allows conversion of peak areas into concentrations for the contaminants of interest. The RF used is recalculated if the standard response varies 25%. If the standard injections vary by more than 25% the standard injections are repeated. If the mean of the two standard injections represents greater than 25% difference then a third standard is injected and a new RF is calculated from the three standard injections. A new data sheet is started with the new RF's and calibration data.

$$\% \text{ difference} = \frac{A \text{ area} - B \text{ area}}{A \text{ area}}$$

Where ; A = mean peak area of standard injection from first calibration
 B = peak area of subsequent standard injection

G) The low ug/L aqueous standards that are made fresh daily need not be refrigerated during the day because they do not change significantly in a 24 hour period. On numerous occasions the unrefrigerated 24 hour old standards have been compared with fresh standards and no difference has



been measurable. If the standards were made at high ppm levels in water, the problem of volatilization would probably be more pronounced in the absence of refrigeration.

H) Primary standards are kept in the hotel room when on a project.

I) A client may provide analytical standards for additional calibration and verification.

II. Syringe Blanks

A) Each uL syringe is blanked before use.

B) 2 cc (glass) syringes will each be blanked if ambient air concentrations are elevated (greater than or equal to 0.01 ug/L) for components of interest.

C) If ambient air concentrations are <0.01 ug/L for components of interest, a representative sample of at least two syringes are blanked at the beginning of each day. If representative syringes have no detectable contamination remaining syringes need not be blanked. If any of representative syringes show contamination, all 2 cc syringes must be blanked prior to use.

D) Syringe blanks are run with air or nitrogen.

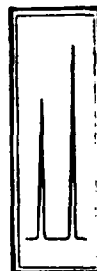
E) If it is necessary for any syringe to be used again before cleaning, it is blanked prior to its second use.

III. System Blanks

A) System blanks are ambient air drawn through the probe and complete sampling apparatus (probe adaptor and 10 cc). The probe is above the ground.

B) One system blank is run at the beginning of each day and compared to a concurrently sampled air analyses.

C) A system blank is run before reusing any sampling system component.



IV. Ambient Air Samples

A) Ambient air samples are collected and analyzed a minimum of two times daily to monitor safety of the work environment and to establish site background concentrations, if any, for contaminants of interest.

B) All ambient air samples shall be documented (Figure 3).

V. Samples

A) All unknown samples will be analyzed at least twice.

B) More unknown samples will be run until reproducibility is within 25%, computed as follows:

$$\text{Difference} = \frac{A - B}{(A + B)/2}$$

Where; A is first measurement result

B is second measurement result

If the difference is greater than .25, a subsequent sample will be run until two measurements are made that have a difference of .25 or less. Those two measurements will be used in the final calculation for that sample.

C) The injection volume should be adjusted so that mass of analyte is as near as possible to that which is contained in the standard, at least within a factor of ten.

D) Whenever possible the attenuation for unknown samples is kept constant through the day (so as to provide a visual check of integrations).

E) A water plug is used as a gas seal in uL syringes

F) A seal is established between syringes when subsampling

G) At very high concentrations air dilutions are acceptable once concentration of contaminants in air have been established.

H) All sample analysis are documented (Figure 3).

I) Separate data sheets are used if chromatographic conditions change

J) Everything is labeled in ug/L, mg/L, etc. PPM and PPB notations are avoided.



VI. Daily System Preparation (Figure 4).

A) Integrators parameters are initialized

1. Pt. evaluation
2. Attenuation
3. Peak markers
4. Auto zero
5. Baseline offset (min. 10% of full scale)

B) The baseline is checked for drift, noise, etc.

C) System parameters are set.

1. Gas flows (Note: N_2 , air, H_2 tank pressure on Page 1 of chromatograms).
2. Temperatures
 - a) Injector
 - b) Column
 - c) Detector

D) After last analysis of the day conditioned septa are rotated into injection ports used during the day and replaced with fresh septa.

E) Column and injector temperatures are run up to bake out residual contamination.

F) Syringes are cleaned each day

1. 2 and 10 cc syringes are cleaned with Alconox or equivalent detergent and brush
2. μ L syringes are cleaned daily with IPA or MeOH and purged with N_2 . Syringe Kleen is used to remove metal deposits in the barrel.
3. Syringes are baked out overnight in the oven of the gas chromatograph at a minimum temperature of 60°C.



VII. Sample Splits

If desired, TRC's clients or any party, with the approval of TRC's client, may use sample splits to verify TRC's groundwater sampling results. Splits of the aqueous standards or the methanol standards used by TRC for instrument calibration may be analyzed by the party requesting sample splits.



Figures 1 through 4

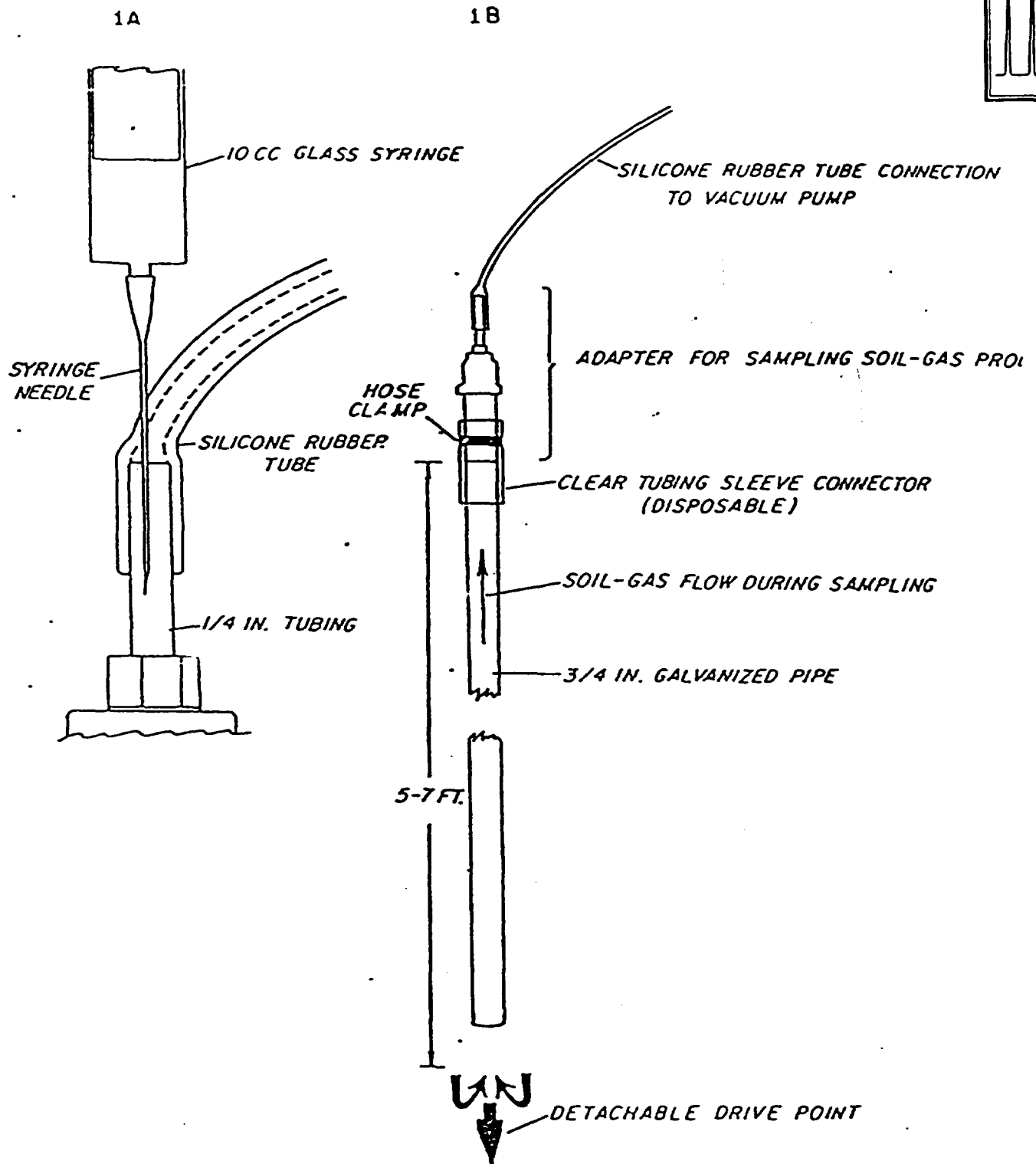


FIGURE 1. SAMPLING APPARATUS

- 1A. CLOSE-UP OF SYRINGE SOIL GAS SAMPLING THROUGH EVACUATION LINE
- 1B. DIAGRAM OF SOIL GAS SAMPLING PROBE WITH ADAPTOR FOR SAMPLING AND EVACUATION OF THE PROBE AFTER IT IS DRIVEN INTO THE GROUND



VAN # 1
PLATE # YCA-274

SOIL GAS INVESTIGATION BACKGROUND INFORMATION

SITE NAME: DAVIDSON CHEMICAL
LOCATION: 14600 WEST AVENUE N., LAMOTHE, SOUTH DAKOTA
DATES OF INVESTIGATION: 2/16-2/18/89
CLIENT NAME & ADDRESS: BLANDENAUER ENVIRONMENTAL
602 HANSEN RD
WYOMING, SD 57667
FIELD REPRESENTATIVE(S) FOR CLIENT: JOE PANDEKOT
PERSON TO WHOM REPORT AND QUESTIONS
SHOULD BE DIRECTED: SARAH NHEDEL
PHONE: (783) 972-1003
CREW: CHEMIST S. CHURLES GEOLOGIST N. KIERWI

REPORT TO INCLUDE (CIRCLE):

- ☒ A. QA/QC-PROCEDURES-DATA ONLY or
☐ B. FULL REPORT WITH CONTOUR MAPS AND INTERPRETATION

PURPOSE OF INVESTIGATION

DETERMINE EXTENT OF CONTAMINATION FROM STORAGE TANK SAIL

TARGET VOCs

<u>TCA</u>		
<u>TLE</u>		
<u>PCE</u>		

GROUNDWATER INFORMATION:

DEPTH TO WATER: 12-16' DIRECTION: NE

SOURCES OF CONTAMINATION

COMPANY USED SOLVENTS IN PHOTO-ETCHING PROCESS IN MANUFACTURE OF
ELECTRONIC CIRCUIT BOARDS. STORAGE TANK LEAKED AND LEACHED FROM
APPROX. 1977-1982 WHEN COMPANY SHUT DOWN. SOURCE WAS REPAIRED
IN 1982

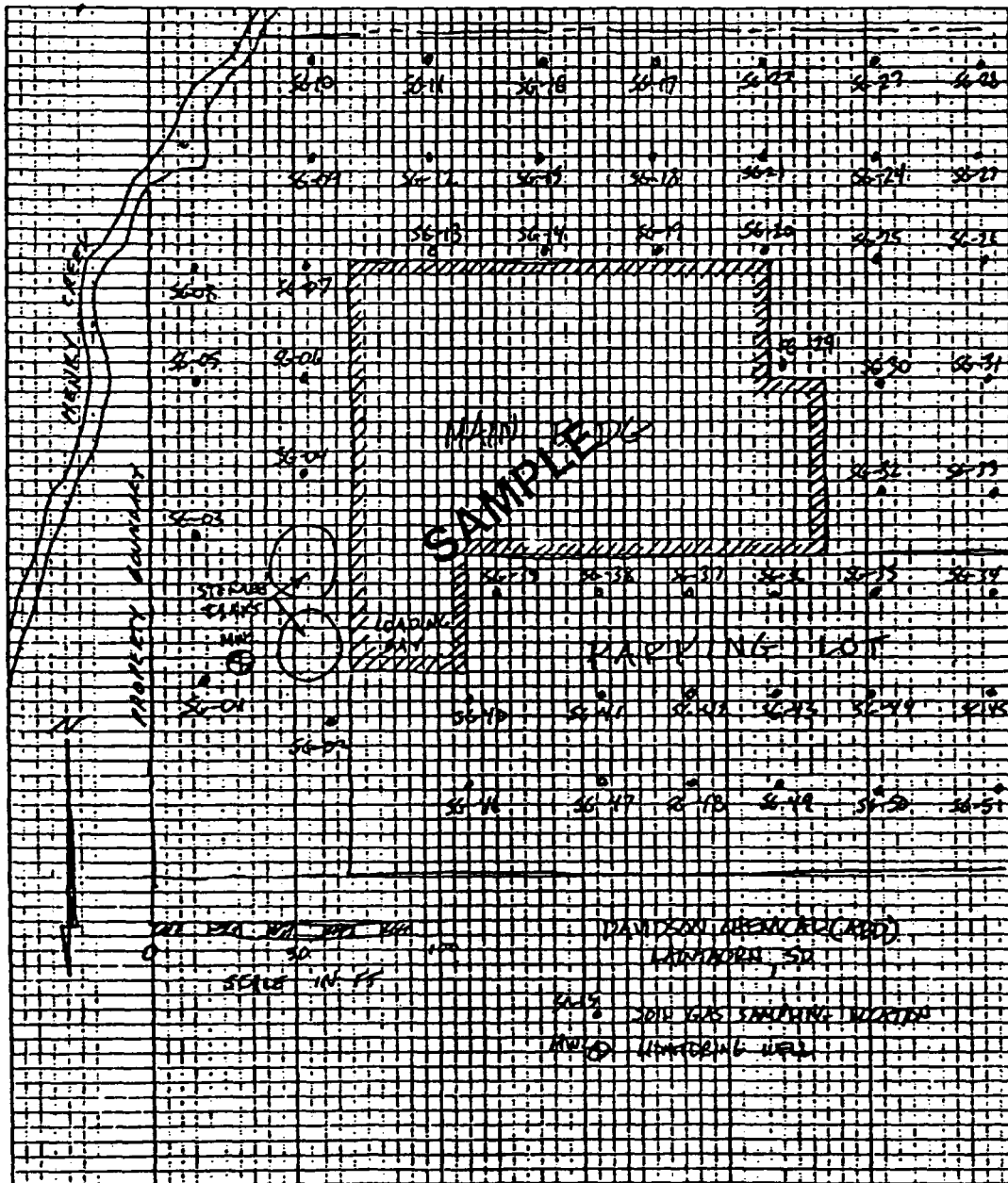
GEOLOGIC SETTING: (e.g. soil type, subsurface geology, etc.)

LOESS & GLACIAL TILL (~10'); FLATBED BASEMENT BELOW 10'

FIGURE 2A
FIELD LOGBOOK - BACKGROUND INFORMATION



SITE MAP



SITE MAPS TO INCLUDE: SITE NAME, SCALE, NORTH ARROW, SOIL GAS LOCATIONS & NUMBERS. CULTURAL AND NATURAL FEATURES TO IDENTIFY

FIGURE 2B
FIELD LOGBOOK - SITE MAP



DATE : 2-16-89
 LOCATION : DAVIDSON CHEMICAL, LANTHORN, SD
 CLIENT : BRANDENBURG ENV.

GC Operator: S. CHARBLES Field Assistant: M. FAVERONI
 Weather : 12°F, SNOW SQUALLS, COLD & WINDY

FIELD HOURS

A Time on site : 0730	Lunch hours : 1
B Time off site : 1730	Downtime hours ¹ : 0
-----	Standby hours ² : 0
Hours on site (B - A) : 10	

DECONTAMINATION

Probe Decontamination	Syringe Decontamination
Total hours: 1/4	Total hours: 1/2
<u>DSK</u> Verified by GC operator	<u>M. Faveroni</u> Verified by field assistant

DAILY SUMMARY

Calibration	Sampling	Analysis
Time start : 0730	Max vacuum : 23 in Hg	Total system
Time end : 0830	Probes used : 13	blanks : 1
-----	Points used : 20	Total air
Total hours: 1	Soil gas samples	samples : 3
	collected : 18	
	Water samples	
	collected : 0	

Field data and gas standards checked by M. Faveroni
 Data checking hours: 1/2

- 1 - Downtime includes time spent repairing sampling & analytic equipment;
 note times and explanation on following field data pages
- 2 - Standby includes time available for sampling but waiting for client;
 note times and explanation on following field data pages

FIGURE 2C
 FIELD LOGBOOK - DAILY SUMMARY

DETECTOR A (0 or 1)
DETECTOR B (0 or 1)
RETENTION TIMES
SAMPLE INJECTION (uL)

COMP 1 0.785

COMP 2 1.15

COMP 3 1.75

STANDARD CONCENTRATION (ug/L):				3 10			3			10		
AREA RESPONSE 1:				95310			2000456			1140876		
FROM INJECTION 2:				103683			1956743			1114123		
3:				107198			2150578			1126578		
RESPONSE FACTOR:				5 -4.90E-16			1.23E-17			4.43E-17		
COMPONENT NAME				F113 2			TCA			TCE		
SAMPLE	TIME(A/B)	INJ A	INJ B	AREA	CONC.	MEAN	AREA	CONC.	MEAN	AREA	CONC.	MEAN
6	11	5	12	14	ERR			ERR			ERR	
H2O BLANK	755			-1000	-0.09797	<0.1	-1000	-0.00245	<0.002	-1000	-0.00885	<.009
7	800	1000		-1000	-0.00048	<0.0005	-1000	-0.00001	<.00001	-1000	-0.00004	<.00004
AIR SAMPLE 8	825	1000		2000	0.000979	0.001	4702	0.000037	.00006	12569	0.000556	0.0006
SYSTEM BLANK 9	845	1000		2000	0.000979	0.001	5560	0.000068	.00007	10724	0.000474	0.0005
SG01-3'	941	1000		15342	0.007515	0.008	5400	0.000066	.00007	351625	0.015560	0.02
SG01-5'	947	1000		17986	0.008811		5874	0.000072		410552	0.018168	
10			13		ERR	15		ERR			ERR	
WS-18	955	1		3424	1.677384	2	-1000	-0.01227	<0.01	40528	1.793498	2
WS-18	1003	1		3650	1.788099		-1000	-0.01227		44715	1.978786	

1. Site and staff information.
2. Name of compound.
3. Concentration of analyte in calibration standard.
4. Peak areas obtained from standard injections during calibration.
5. Response factor (RF) for compound obtained from three calibration runs. The RFs are used for calculation of actual concentrations and are included on each data sheet.
6. Water blank verifies purity of standard water and cleanliness of injection system.
7. Nitrogen blank verifies decontamination of syringes and analytical equip.
8. Air sample gives ambient concentrations for comparison with system blank.

9. System blank verifies decontamination of sampling equipment.
10. Sample ID number; 0001-0' (cell gas sample 1 taken 0' below grade), 45-10 (water sample).
11. Time of analysis identifies the chromatogram from which the data was taken.
12. Amount of sample injection - used for concentration calculation.
13. Peak area - raw data produced by the computing integrator that is proportional to the mass of analyte in the sample.
14. Actual concentration present in the sample rounded to 1 significant figure.
15. Mean concentration of duplicate injections.



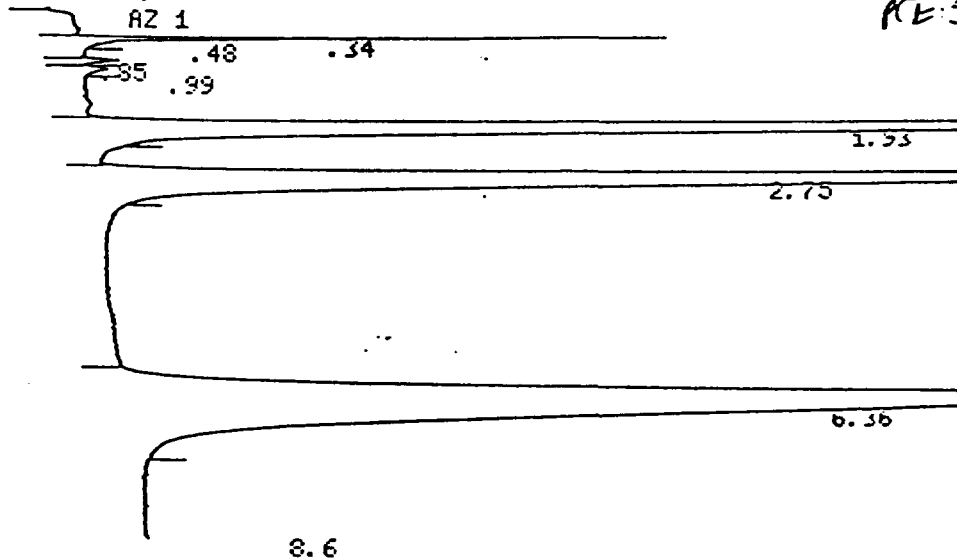
READY
 DATE " 01-27-89
 TIME " 15:36
 FI= 1. FE= 1. MN= 0.
 PRESS 'ENTER' TO SKIP ENTRY
 FILE NAME=" STD
 TIME FUNCTION VALUE
 TT= .01 TF=" AZ TV= 1
 TT= .01 TF=" PM TV= 1
 TT=

Column <u>OV-101</u>	Detector <u>ECD</u>
Length <u>6'</u>	Voltage <u>34.26</u>
Dia. <u>1/8"</u>	Sensit. <u> </u>
Liquid Phase <u>OV-101</u>	Flow Rates, ml/min <u> </u>
Wt. % <u>10</u>	Hydrogen <u> </u> Air <u> </u>
Support <u>Chromosorb W</u>	Scavenge <u> </u>
Mesh <u>60/80</u>	Split <u> </u>
Carrier Gas <u>N₂</u>	Temperature, °C <u> </u>
Rotameter <u>80</u>	Det. <u>350</u> Inj. <u>250</u>
Inlet Press <u>25</u> psig	Column Initial <u>50</u> <u>150</u>
Rate <u>30</u> ml/min	Final <u> </u>
CHART SPEED <u>1</u>	Rate <u> </u>
SAMPLE <u> </u>	Solvent <u> </u>
Size <u> </u>	Concn. <u> </u>
Operator <u>John Chemist</u>	Date <u>1-27-89</u>

METHOD NUMBER: MN=

END OF DIALOG
 AT= 32
 OF=20
 PT=1000

CHANNEL A INJECT 01-27-89 15:43:04



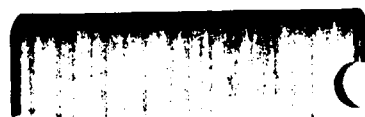
50°C STD 5ml TCA'S
 TCE: 10/19/L
 RE: 5

STD 01-27-89 15:43:04 CH= "R" PS= 1.

FILE 1.	METHOD 0.	RUN 1	INDEX 1
PEAK#	AREA%	RT	AREA BC
1	0.377	0.34	13779 02
2	1.754	0.48	64194 03
3	0.164	0.85	6011 01
4	0.152	0.99	5547 01
5	25.081	1.93	917708 01
6	26.951	2.75	986147 01
7	45.521	6.36	1665628 01
TOTAL	100.		3659014

FIGURE 4
 CHROMATOGRAM DOCUMENTATION

(



)

APPENDIX B-4

DISSOLVED OXYGEN ANALYSIS OF GROUNDWATER

YSI DISSOLVED OXYGEN METER AND PROBE

Scope and Application: The instructions outlined below are to be followed for the daily calibration and routine operation of the YSI Dissolved Oxygen Meter and Probe.

Reference: Instruction Manual YSI Model 54ARC Dissolved Oxygen Meter and YSI 5700 Dissolved Oxygen Probe.

Reagents and Apparatus:

1. YSI 54ARC Dissolved Oxygen Meter
2. YSI 5720A B.O.D. Bottle Probe
3. Membrane and KCl kit, standard, YSI 5775
4. Replacement "O" ring, YSI Part #5945
5. Beater boot assembly, YSI Part #5486

Operating Procedure:

I. Preparing the Probe

All YSI 5700 Series Probes have similar sensors and should be cared for in the same manner. They are precision devices relying on good treatment if high accuracy measurements are to be made. Prepare the probe as follows.

ALL PROBES ARE SHIPPED DRY - FOLLOW THESE INSTRUCTIONS TO PREPARE FOR USE

1. Prepare the electrolyte by dissolving the KCl crystals in a dropper bottle with Milli-Q water. Fill the bottle to the top.
2. Remove the "O" ring and membrane. Thoroughly rinse the sensor with KCl solution.
3. Fill the probe with electrolyte as follows (see Figure 1):
 - a. Grasp the probe with your left hand.
 - b. Fill the sensor body until no more air bubbles appear. Tap the probe against the countertop to dislodge any air bubbles adhering to the sensor.
 - c. Secure a membrane under your left thumb. Add more electrolyte to the probe until a large meniscus completely covers the gold cathode. NOTE: Handle membrane material with care, keeping it clean and dust free, touching it only at the ends.
 - d. With the thumb and forefinger of your other hand, grasp the free end of the membrane.

- e. Using a continuous motion stretch the membrane UP, OVER, and DOWN the other side of the sensor. Stretching forms the membrane to the contour of the probe. The membrane can be stretched to approximately 1 1/2 times its normal size.
 - f. Secure the end of the membrane under the forefinger of the hand holding the probe.
 - g. Roll the "O" ring over the end of the probe. There should be no wrinkles in the membrane or trapped air bubbles. Some wrinkles may be removed by lightly tugging on the edges of the membrane beyond the "O" ring.
 - h. Trim off excess membrane with scissors or sharp knife. Check that the stainless steel temperature sensor is not covered by excess membrane.
4. Shake off excess KCl.
 5. Store the probe in a BOD bottle containing about 1 inch of water.
 6. Membranes average replacement is 2-4 weeks. If the electrolyte in the probe is allowed to evaporate, air bubbles form under the membrane. If air bubbles are noted under the membrane or if the membrane becomes damaged, thoroughly flush the reservoir with fresh KCl and install a new membrane as described above.
 7. Replace the membrane if erratic readings are observed or if calibration is not stable.

NOTE: The gold cathode should always be bright and untarnished. If it is tarnished (which can result from contact with certain gases) or plated with silver (which can result from extended use with a loose or wrinkled membrane), return it to the factory for service. Never use chemicals or abrasives in an attempt to clean it.

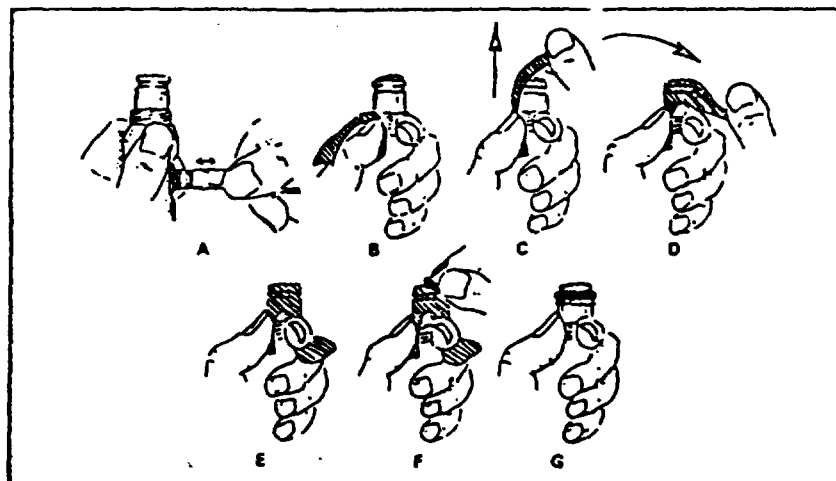


Figure 1

II. Preparing the YSI Instrument

It is important that the instrument be placed in the intended operating position; vertical, tilted, or on its back - before it is prepared for use and calibrated. (See Figure 8). Recalibration may be necessary when the instrument operating position is changed. After preparing the probe proceed as follows:

1. With switch in the OFF position, adjust the meter pointer to Zero with the screw in the center of the meter panel. Readjustment may be necessary if the instrument operating position is changed.
2. Switch to RED LINE and adjust with the RED LINE knob until the meter needle aligns with the red mark at the 31°C position.
3. Switch to ZERO and adjust to zero with zero control knob.
4. Attach the prepared probe to the PROBE connector of the instrument and adjust the retaining ring finger tight.
5. For optimum probe stabilization, let the meter and probe equilibrate for 15 minutes before calibrating.

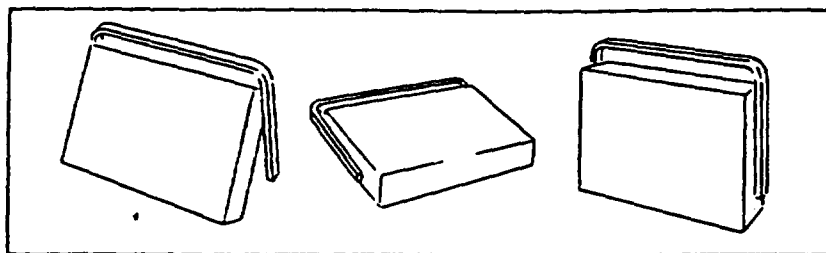


Figure 2

III. Calibration

The operator has a choice of three calibration methods: Winkler titration, Saturated Water, and Air. The three methods are described in the following paragraphs. The Winkler titration is the preferred method of calibration.

Winkler Titration

1. Determine the dissolved oxygen in two samples from the aerated water source using the Winkler titration technique (refer to the Dissolved Oxygen SOP) and average the values. If the values differ by more than 0.5 mg/L, discard the samples and repeat.

2. Place the YSI probe in the third sample and stir.
3. Switch to desired mg/L scale range and adjust with the CALIBRATION control to the average value determined in Step 1. Allow the probe to remain in the sample for at least two minutes before setting the calibration value, and leave in the sample for an additional 2 minutes to verify stability (Readjust if necessary).

Saturated Water Calibration

1. Air saturate a volume of water by aerating for at least 1 hour at a constant temperature (preferably room temperature).
2. Place the probe in the sample and stir. Switch to TEMPERATURE scale. Refer to Calibration Table I for the mg/L value corresponding to the temperature.
3. Determine local altitude or the "true" atmospheric pressure (note that "true" atmospheric pressure is as read on a barometer. Weather Bureau reporting of atmospheric pressure is corrected to sea level). Using Calibration Table II determine the correction factor for your pressure or altitude.
4. Multiply the mg/L value from Table I by the correction factor from Table II to determine the corrected calibration value for your conditions.

EXAMPLE: Assume temperature = 21°C and altitude = 1000 feet. From Table I the calibration value for 21°C is 8.9 mg/L. From Table II the correction factor for 1000 feet is about 0.96. The corrected calibration value is $8.9 \text{ mg/L} \times 0.96 = 8.54 \text{ mg/L}$.

5. Switch to an appropriate mg/L scale range and adjust the CALIBRATE knob while stirring until the meter reads the corrected calibration value from Step 4. Leave the probe in the sample for two minutes to verify calibration stability. Readjust if necessary.

Air Calibration - Fresh Water

1. Place the probe in a BOD bottle partially filled with water. Wait approximately 10 minutes for temperature stabilization. This may be done simultaneously while the probe is stabilizing.
2. Switch to TEMPERATURE and read. Refer to Table I - Solubility of Oxygen in Fresh Water, and determine calibration value.
3. Determine altitude or atmospheric correction factor using Table II.

4. Multiply the calibration value from Table I by the correction factor from Table II.

EXAMPLE: Assume temperature = 21°C and altitude = 1000 feet. From Table I the calibration value for 21°C is 8.9 mg/L. From Table II the correction factor for 1000 feet is about 0.96. Therefore the corrected calibration value is $8.9 \text{ mg/L} \times 0.96 = 8.54 \text{ mg/L}$.

5. Switch to an appropriate mg/L range and adjust the CALIBRATE knob until the meter reads the corrected calibration value from Step 4. Wait two minutes to verify calibration stability. Readjust if necessary.

IV. Dissolved Oxygen Measurement

1. With the instrument prepared for use and the probe calibrated, place the probe in the sample to be measured and turn on stirring boot.
2. Allow sufficient time for probe to stabilize to sample.
3. Read dissolved oxygen directly from scale.

V. Maintenance of the Stirrer Boot

1. The probe uses a flexible stirring boot to transmit motion from the sealed motor housing to the sample. If the boot shows signs of cracking or other damage which may allow leaking into the motor housing, the boot must be replaced.
2. In fresh water applications boot life is normally several years, but this may be shortened by exposure to hydrocarbons, moderate to strong acids or bases, ozone, or direct sunlight. For maximum life rinse the boot with deionized water after use in contaminated samples.
3. Boot replacement is as follows:
 - a. Pull off old assembly and clean shaft.
 - b. Slide on new assembly making sure the back spring is on the grooved area of the shaft. A small amount of rubber cement may be used.
 - c. Check that there is sufficient clearance between the tip and the end of the shaft to permit turning without binding.

TABLE I
Solubility of Oxygen in Fresh Water

Temperature °C	mg/L Dissolved Oxygen	Temperature °C	mg/L Dissolved Oxygen
0	14.60	23	8.56
1	14.19	24	8.40
2	13.81	25	8.24
3	13.44	26	8.09
4	13.09	27	7.95
5	12.75	28	7.81
6	12.43	29	7.67
7	12.12	30	7.54
8	11.83	31	7.41
9	11.55	32	7.28
10	11.27	33	7.16
11	11.01	34	7.05
12	10.76	35	6.93
13	10.52	36	6.82
14	10.29	37	6.71
15	10.07	38	6.61
16	9.85	39	6.51
17	9.65	40	6.41
18	9.45	41	6.31
19	9.26	42	6.22
20	9.07	43	6.13
21	8.90	44	6.04
22	8.72	45	5.95

Source: Derived from 16th Edition "Standard Methods for the Examination of Water and Wastewater".

This table shows the amount of oxygen in mg/L that is dissolved in air saturated fresh water at sea level (760 mm Hg atmospheric pressure) as temperature varies from 0° to 45°C.

Table II
Correction for Atmospheric Pressure

Atmospheric Pressure mm/Hg	or	Equivalent Altitude Ft.	=	Correction Factor
775		540		1.02
760		0		1.00
745		542		.98
730		1094		.96
714		1628		.94
699		2274		.92
684		2854		.90
669		3466		.88
654		4082		.86
638		4756		.84
623		5403		.82
608		6065		.80
593		6744		.78
578		7440		.76
562		8204		.74
547		8939		.72
532		9694		.70
517		10472		.68
502		11273		.66

Source: Derived from 16th Edition "Standard Methods for the Examination of Water and Wastewater".

This table shows the correction factor that should be used to correct calibration value for the effects of atmospheric pressure or altitude. Find true atmospheric pressure in the left hand column and read across to the right hand column to determine the correction factor. (Note that "true" atmospheric pressure is as read on a barometer. Weather Bureau reporting of atmospheric pressure is corrected to sea level.) If atmospheric pressure is unknown, the local altitude may be substituted. Select the altitude in the center column and read across to the right hand column for the correction factor.

YSI 5700 SERIES DISSOLVED OXYGEN PROBES INSTRUCTIONS

The probes described in these instructions are designed for direct use with YSI Models 50, 51B, 54ABP, 54ARC, 56, 57 and 58 Dissolved Oxygen Meters. The probes can also be used with discontinued YSI Models 51A, 54BP and 54RC Dissolved Oxygen Meters when the YSI 5735 Cable Adapter is employed.

PRINCIPLES OF OPERATION

YSI 5700 Series Probes are polarographic sensors. A thin permeable membrane stretched over the sensor isolates the electrodes from the environment, but allows oxygen to enter. When a polarizing voltage is applied across the sensor, oxygen that has passed through the membrane reacts at the cathode, causing a current to flow.

The membrane passes oxygen at a rate proportional to the difference across it in partial pressure of oxygen. Since oxygen is rapidly consumed at the cathode, it can be assumed that the oxygen pressure under the membrane is zero. Hence, the force causing the oxygen to diffuse through the membrane is proportional to the partial pressure of oxygen outside the membrane. As the oxygen partial pressure varies, both the oxygen diffusion through the membrane and the probe current will change proportionally.

SPECIFICATIONS

Cathode: Gold

Anode: Silver

Membrane: .001" FEP Teflon, standard

Electrolyte: Half saturated KCl

Temperature Range: -5° to 45°C

15° to 35°C for the 5760 probe

Temperature Accuracy: $\pm 0.2^\circ\text{C}$

Temperature Compensation: (see instrument specifications)

Polarizing Voltage: 0.8 Volts (nominal)

Probe Current in Air at 30°C: 19 microamps (nominal)

in Nitrogen at 30°C: 0.15 microamps or less

Response Time: Typical response for dissolved oxygen, using standard membranes, is 90% in 10 seconds at a constant temperature of 30°C.

Response at low dissolved oxygen levels is typically 90% in 30 seconds.

ACCESSORIES AND REPLACEMENT PARTS

YSI 5492A Battery Pack for Models 51B and 54A (Powers the submersible stirrers.)

YSI 5735 Cable Adapter: (Mates 5700 Series probes with discontinued YSI Models 51A, 54BP and 54RC Dissolved Oxygen Meters)

Accessories for the 5720A, 5739 and 5750

YSI 5680 Probe Reconditioning Kit. Includes a sanding tool and ten adhesive disks.

YSI 5775 Membrane and KCl Kit, Standard. Includes two 15-membrane packets (.001" thick standard FEP Teflon membranes) and a 30 ml bottle of KCl with Kodak Photo Flo.

YSI 5776 Membrane and KCl Kit, High Sensitivity. Includes two 15-membrane packets (.0005" thick FEP Teflon membranes) and a 30 ml bottle of KCl with Kodak Photo Flo. Used for measurements below 15°C and/or for low oxygen levels

YSI 5793 .001" membranes, 10-membrane packet

YSI 5794 .0005" membranes, 10-membrane packet

YSI 5945 O-ring pack (Contains replacement sensor O-rings)

Accessories for the 5720A Only

YSI 5486 Stirrer Boot Assembly

Accessories for the 5739 Only

YSI 5075A Calibration Chamber

YSI 5986 Diaphragm Kit

YSI 5740-10 detachable 10' cable

YSI 5740-25 detachable 25' cable

YSI 5740-50 detachable 50' cable

YSI 5740-100 detachable 100' cable

YSI 5740-150 detachable 150' cable

YSI 5740-200 detachable 200' cable

YSI 5791A Submersible Stirrer with 50' cable for stirrer only

YSI 5795A Submersible Stirrer with 50' combined probe and stirrer cable

YSI 5720A BOD BOTTLE PROBE

The 5720A bottle probe (Figure 1) is used for measuring dissolved oxygen in standard BOD bottles. It is provided with a stirrer powered by a DC supply available for 115 or 230 VAC input.

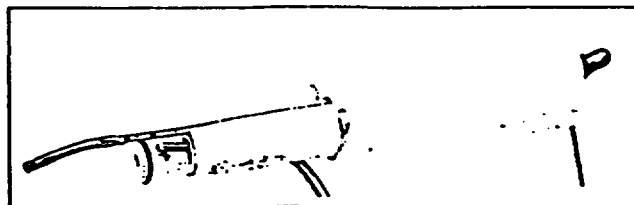


Figure 1. The YSI 5720A Probe



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To use the 5720A, plug the stirrer power supply into line power and the probe plug in the instrument. With the stirrer off, place the tapered probe end into a filled the BOD bottle and turn on the stirrer. The probe should be operated with a minimum of trapped air in the bottle. A slight amount of air in the unstirred region at the top may be neglected, but no bubble should be permitted around the sensor. CAUTION: The motor housing is not waterproof; do not submerge this probe beyond the part that is inserted into a BOD bottle.

Stirrer Boot (YSI 5486)

The 5720A uses a flexible stirring boot to transmit motion from the motor housing to the sample. If the boot shows signs of cracking or other damage liable to allow leakage into the motor housing, it must be replaced. Running the 5720A with a damaged stirring boot could cause permanent motor damage. Boot life may be shortened by exposure to hydrocarbons, moderate to strong acids or bases, ozone, or direct sunlight. For maximum life, rinse the boot after each use. Boots are replaced as follows:

1. Pull off the old assembly and clean the stir rod housing.
2. Slide on the new assembly, making sure the back spring is over the grooved area of the stir rod housing. A drop of alcohol will aid installation by providing lubrication.
3. Do not permit the stir rod to press against the end of the stirrer boot tip or it will bind.

YSI 5739 DISSOLVED OXYGEN PROBE

The 5739 probe system consists of the probe body plus a detachable cable (see Figure 2). The detachable cable is a convenience feature that facilitates changing cable lengths and replacing damaged cables or probes. The probe and cable assembly is held together with a threaded retainer. The assembly is not intended for casual disconnection; cable and probe should be separated only when necessary.

To detach the cable, unscrew the retainer and slide it down the cable to expose the connector. Pull gently on the connector until it comes away from the probe body. If the O-ring is frayed or damaged, replace it: a replacement O-ring is supplied with each 5740 cable. Reassemble by pushing the connector into the probe body, rotating it until the two halves mate. A light coating of silicone grease on the O-ring will make reassembly easier. Be sure the connector is dry; otherwise, erratic readings may result. Screw on the retainer finger-tight only.

Pressure Compensation

The 5739 probe has a unique pressure compensating system that helps assure accurate readings at great depths. Pressure compensation is effective to 1/2% of reading with pressures up to 100 psi (230 feet of water). The compensating system does not normally require service and should not be taken apart. However, if electrolyte is leaking through the diaphragm, or if there is an obvious puncture, the diaphragm must be replaced. A spare is supplied with the probe. Use a coin to unscrew the retaining plug and remove the washer and diaphragm. With distilled water, flush any salt crystals from the reservoir, install a new diaphragm (flat side out), replace the washer and securely screw in the retaining plug.

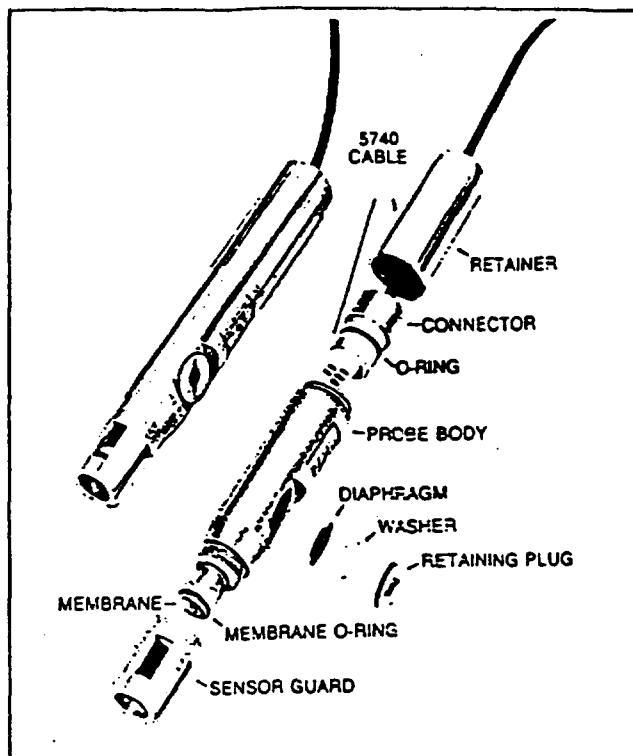


Figure 2. The YSI 5739 Probe

YSI 5750 BOD BOTTLE PROBE

The 5750 (Figure 3) is similar to the 5720A except that it does not have a stirrer. Agitation of the sample must be provided by other means, such as a magnetic stirrer.

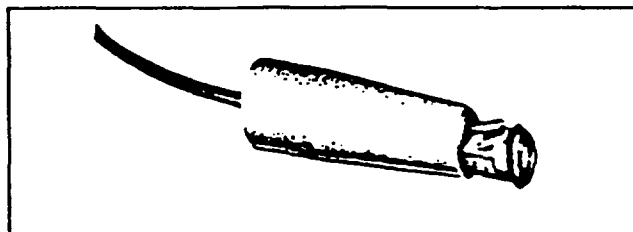


Figure 3. The YSI 5750 Probe

PROBE PREPARATION

All probes are shipped dry. You must follow these instructions when preparing a new probe or when changing membranes. Prepare the electrolyte by dissolving the KCl crystals which are supplied in a dropper bottle that should be filled to the neck with distilled water and shaken until the crystals are dissolved.

1. Unscrew the sensor guard (5739 only). Remove the O-ring and membrane, then thoroughly rinse the sensor with distilled water.
2. To fill the probe with electrolyte and install a new membrane, follow these steps:
 - a. Grasp the probe in your left hand. (See the sketches in Figure 4.) When preparing the 5739 probe, the pressure compensating port should be to the right. Successively fill the sensor body with electrolyte while pumping the diaphragm with the eraser end of a pencil or a similar soft, blunt tool. Continue filling and pumping until no more

air bubbles appear. For ease in preparing the 5720A, the stirring rod should be to the left. When preparing the 5720A or 5750 probes, simply fill the sensor body until no more air bubbles appear.

- b. Secure a membrane between your left thumb and the probe body. Add more electrolyte to the probe until a large meniscus completely covers the gold cathode. **NOTE:** Handle membrane material with care, touching it at the ends only.
- c. With the thumb and forefinger of your other hand, grasp the free end of the membrane.
- d. With a continuous motion, stretch it up, over and down the other side of the sensor. Stretching forms the membrane to the contour of the probe.
- e. Secure the end of the membrane under the forefinger of your left hand while holding the probe.
- f. Roll the O-ring over the end of the probe, being careful not to touch the membrane surface. For the 5720A, start at the right side of the sensor and roll the O-ring toward the stirring rod. There should be no wrinkles in the membrane or trapped air bubbles. Some wrinkles may be removed by lightly tugging on the edges of the membrane beyond the O-ring.
- g. Trim off excess membrane with scissors or sharp knife. Check that the stainless steel temperature sensor is not covered by excess membrane.
3. Shake off excess KCl. On the 5739, reinstall the sensor guard.

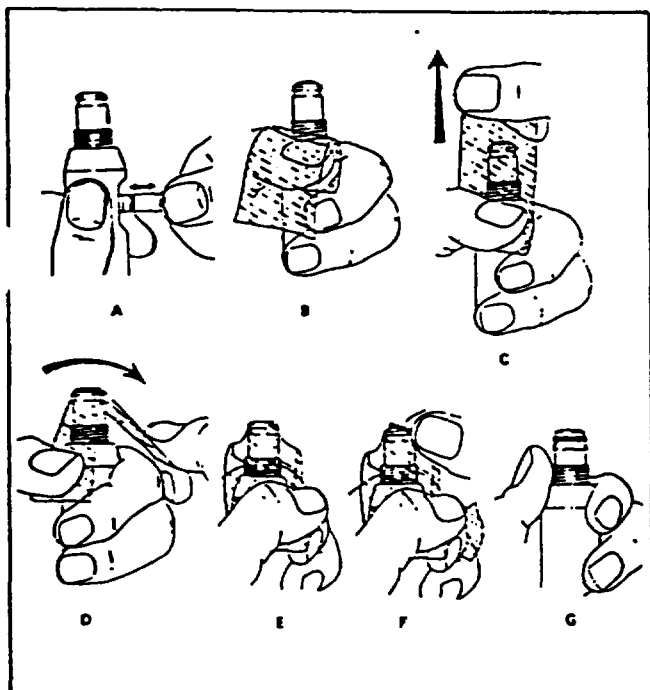


Figure 4. Membrane Application

Probe Storage

A bottomless plastic bottle is provided with the YSI 5739 probe for convenient storage. Place a small piece of moist towel or sponge in the bottle and insert the probe into the open end. This keeps the electrolyte from drying out. The 5720A and 5750 probes can be stored in a BOD bottle containing at least 1" of water.

OPERATING PRECAUTIONS, ALL PROBES

1. Membrane life depends on use. Membranes will last a long time if installed properly and treated with care during use. Erratic readings result from loose, wrinkled or fouled membranes, or from large bubbles in the electrolyte reservoir. If erratic readings, or evidence of membrane damage occur, you should replace the membrane and KCL. The average replacement interval is two to four weeks; electrolyte in constant or heavy use will be exhausted in about two weeks.

If the sensor O-ring on any probe is worn or loose, replace it with the O-ring provided in the YSI 5545 O-ring Pack.

2. The gold cathode should always be bright and untarnished. If it is tarnished (which can result from contact with certain gases) or plated with silver (which can result from extended use with a loose or wrinkled membrane), it needs to have its surface restored. Probes may either be returned to the factory, or cleaned with the YSI 5680 Probe Reconditioning Kit; never use chemicals or any abrasive not supplied with this kit.

3. It is also possible that the silver anode may become contaminated, which will prevent successful calibration. Try soaking the probe overnight in a 3% ammonia solution; rinse with deionized water, recharge with electrolyte, and install a new membrane. If still unable to calibrate after several hours, return the probe for service.

4. Hydrogen sulfide, sulfur dioxide, halogens, and nect are interfering gases. If you suspect erroneous readings, it may be necessary to determine if these are the cause.

These gases have been tested for response:

100% Carbon Monoxide	less than 1%
100% Carbon Dioxide	around 1%
100% Hydrogen	less than 1%
100% Chlorine	2/3 O ₂ response
100% Helium	none
100% Nitrous Oxide	1/3 O ₂ response
100% Ethylene	none
100% Nitric Oxide	1/3 O ₂ response

5. The correct liquid level in BOD bottles is achieved by overfilling, then inserting a stopper and pouring off the excess. When using a YSI 5760 or a 5720A probe in a filled BOD bottle, be careful to insert it slowly to avoid sample overflow.

6. When using the 5720A in samples containing heavy particulate solids, additional stirring may be needed. Inverting the stoppered bottle immediately before use will usually provide adequate mixing.

CALIBRATION

Daily calibration is generally appropriate. Calibration can be disturbed by physical shock, touching the membrane, fouling of the membrane or drying out of the electrolyte. Check calibration after each series of measurements, and in time you will develop a realistic schedule for recalibration. When probes are not in use, store them as recommended in Probe Preparation.

Probes may be calibrated by Winkler Titration or by the Water Saturated Air method. Experience has shown that air calibration is quite reliable, yet far simpler than titration. Both methods are described here. Consult the manual for your particular instrument for more complete instructions.

Winkler Titration

1. Draw a volume of water from a single source and carefully divide it into four samples. Determine the oxygen in three of the samples using the Winkler Titration technique and average the three values. If one of the values differs from the other two by more than 0.5 mg/L, discard it and average the two values remaining.

2. Using the probe-meter system you are calibrating, place the probe into the fourth sample and stir.

3. Switch to the desired mg/L range and adjust the CALIBRATION control to the average value determined in step 1. Allow the probe to remain in the sample for at least 5 minutes before setting the calibration value, then leave it in the sample for an additional two minutes to verify stability. Readjust if necessary.

Air Calibration

1. Place the probe in a BOD bottle containing about 1 inch of water. Wait approximately ten minutes for temperature stabilization.

The 5739 probe can be placed in the YSI 5075A Calibration Chamber or in the small calibration bottle supplied with the probe (the one with the hole in the bottom) along with a few drops of water, or a moistened towel or cloth.

2. Read the temperature and refer to the instrument Calibration Table to determine the calibration value.
NOTE: To achieve the stated accuracy of measurement, the probe must be stabilized before calibrating. The calibration temperature should be within 5 degrees of the sample temperature.

3. Determine the atmospheric correction factor (see Instrument instructions).

4. Multiply the calibration value by the correction factor.

5. Switch your instrument to an appropriate mg/L range and adjust the CALIBRATE control until the meter reads the corrected calibration value from step 4. Without changing the calibration setup, monitor the readings for an additional 3 minutes to verify calibration stability. Readjust if necessary.

WARRANTY AND REPAIR

All YSI products carry a one-year warranty on workmanship and parts, exclusive of batteries. Damage through accident, misuse, or tampering will be repaired at a nominal charge, if possible, when the item is returned to the factory or to an authorized YSI dealer. Electrode cleaning is not covered by warranty.

If you are experiencing difficulty with any YSI product, it may be returned for repair, even if the warranty has expired. YSI maintains complete facilities for prompt servicing on all its products. This warranty is limited to repair or replacement (YSI's option) at no charge.



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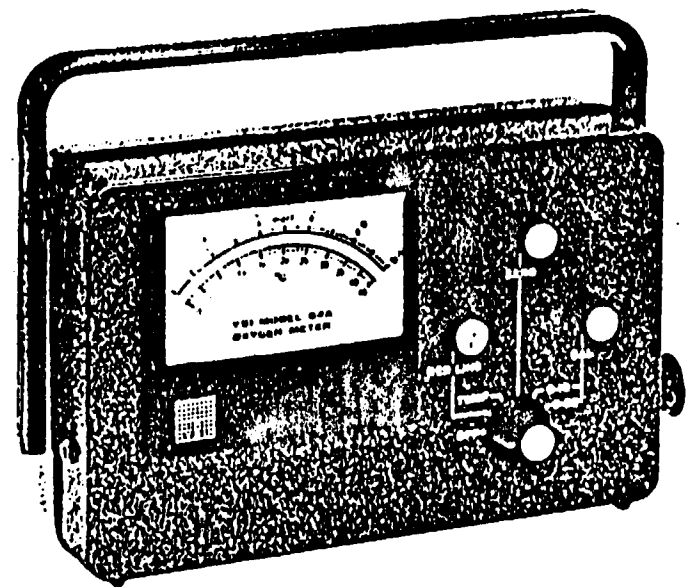
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**INSTRUCTION MANUAL
YSI MODELS 54ARC AND 54ABP
DISSOLVED OXYGEN METERS**



Scientific Division
Yellow Springs Instrument Co., Inc.
Yellow Springs, Ohio 45387, U.S.A. • Phone 513-767-7241

SUMMARY OF OPERATING INSTRUCTIONS

1. CALIBRATION

- A. Switch instrument to OFF and adjust meter mechanical zero.
- B. Switch to RED LINE and adjust.
- C. Prepare probe for operation, connect to instrument, wait up to 15 minutes for probe to stabilize. Probe can be in calibration chamber or ambient air.
- D. Switch to ZERO and adjust to "0" on mg/l scale.
- E. Switch to TEMP and read on °C scale.
- F. Use probe temperature and true local atmospheric pressure (or feet above sea level) to determine calibration values from Tables I and II. (See pages 14 and 15).

EXAMPLE: Probe temperature = 21°C; Altitude = 1000 feet. From Table I the calibration value for 21°C is 8.9 mg/l. From Table II the altitude factor for 1000 feet is approximately .96. The correct calibration value, then, is:

$$8.9 \text{ mg/l} \times .96 \text{ factor} = 8.54 \text{ mg/l}$$

- G. Switch to 0-10 or 0-20 mg/l range and adjust meter with CAL control to calibration value determined in Step F.

NOTE: It is desirable to calibrate probe in a high humidity environment. (See calibration section for more detail).

2. MEASUREMENT

- A. Place probe in sample and stir.
- B. Allow sufficient time for probe to stabilize to sample temperature and dissolved oxygen.
- C. Read dissolved oxygen on appropriate range (1-10 or 0-20 mg/l)
- D. We recommend the instrument be left on between measurements to avoid the necessity to repolarize the probe.

3. GENERAL CARE

- A. Recharge batteries in the YSI Model 54ARC when the instrument can no longer be red lined. Recharge 16-20 hours. Replace with Burgess CD-6 or equivalent. Replace batteries in the YSI Model 54ABP when red line cannot be set with Panasonic UM-2N or equivalent.
- B. Membranes will last indefinitely, depending on usage. Average replacement is 2-4 weeks. Probe should be stored in humid environment to prevent drying out.
- C. Calibrate daily.

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GENERAL DESCRIPTION

The YSI Models 54ARC and 54ABP Dissolved Oxygen Meters are intended for dissolved oxygen and temperature measurement in water and wastewater applications, but are also suitable for use in certain other liquids. Dissolved Oxygen is indicated in mg/l (milligrams per liter) on 0-10 and 0-20 mg/l scales. Temperature is indicated in °C on a -5° to +45°C scale. Both dissolved oxygen ranges are automatically temperature compensated for solubility of oxygen in water and permeability of the probe membrane.

The probes use Clark-type membrane covered polarographic sensors with built-in thermistors for temperature measurement and compensation. A thin, permeable membrane stretched over the sensor isolates the sensor elements from the environment, but allows oxygen and certain other gases to enter. When a polarizing voltage is applied across the sensor, oxygen that has passed through the membrane reacts at the cathode, causing a current to flow.

The membrane passes oxygen at a rate proportional to the pressure difference across it. Since oxygen is rapidly consumed at the cathode, it can be assumed that the oxygen pressure inside the membrane is zero. Hence, the force causing the oxygen to diffuse through the membrane is proportional to the absolute pressure of oxygen outside the membrane. If the oxygen pressure increases, more oxygen diffuses through the membrane and more current flows through the sensor. A lower pressure results in less current.

Power to operate the system is provided by internal batteries in the instruments, rechargeable batteries in the YSI Model 54ARC and disposable batteries in the YSI Model 54ABP.

SPECIFICATIONS

I. Instrument

Oxygen Measurement

Ranges: 0-10 and 0-20 mg/l (0-5 and 0-10 mg/l with YSI 5776 High Sensitivity Membrane)

Accuracy: $\pm 1\%$ of full scale at calibration temperature (± 0.1 mg/l and 0-10 scale).

Readability: .05 mg/l on 0-10 scale; 0.1 mg/l on 0-20 scale.

Temperature Measurement

Ranges: -5° to +45°C

Accuracy: $\pm 0.7^\circ\text{C}$, including probe

Readability: 0.25°C

Temperature Compensation

$\pm 1\%$ of D.O. reading for measurements made within $\pm 5^\circ\text{C}$ of calibration temperature.

$\pm 3\%$ of D.O. reading over entire range of -5 to +45°C Probe temperature.

System Response Time

Typical response for temperature and D.O. readings is 90% in 10 seconds at constant temperature of 30°C with YSI 5775 Membranes. D.O. response at low temperature and low D.O. is typically 90% in 30 seconds. YSI 5776 High Sensitivity Membranes can be used to improve response at

low temperature and low D.O. concentrations. If response time under any operating conditions exceeds two minutes, probe service is indicated.

Operating Temperature Range

Instrument and probe operating range is -2° to +45°C. Large ambient temperature changes will result in 2% loss of accuracy unless Red Line and Zero are reset.

Recorder Output

0 to 114-136 mV. Recorder should have 50,000 ohms minimum input impedance.

Power Supply

YSI Model 54ABP: (4) 1.5 volt carbon zinc batteries provide approximately 1000 hours operation. Replace with Panasonic UM-2N or equal.

YSI Model 54ARC: (4) 1.25 volt Ni-Cad rechargeable cells (Burgess CD-6 or equal) provide approximately 100 hours of operation between charges.

II. Probe

Cathode: Gold

Anode: Silver

Membrane: .001" FEP Teflon (.0005" FEP Teflon available)

Electrolyte: Half Saturated KCl

Temperature Compensation: (See SPECIFICATIONS, I. Instrument)

Pressure Compensation: Effective 1/2% of reading to pressures of 100 psi (230 ft. water)

Polarizing Voltage: 0.8 volts nominal

Probe Current: Air at 30°C = 19 microamps nominal

Nitrogen at 30°C = .15 microamps or less

III. Accessories and Replacement Parts

YSI 5720A — Self Stirring B.O.D. Bottle Probe

YSI 5750 — Non Stirring B.O.D. Bottle Probe

YSI 5739 — Oxygen Temperature Probe for field use. Combine with one of the following cables for desired lead length:

YSI 5401 — Battery Charger Eliminator 115V

YSI 5402 — Battery Charger Eliminator 230V

Detachable leads for use with YSI 5739:

YSI 5740-10	10' cable
YSI 5740-25	25' cable
YSI 5740-50	50' cable
YSI 5740-100	100' cable
YSI 5740-150	150' cable
YSI 5740-200	200' cable

YSI 5492A — Battery Pack Operates YSI 5791A and 5795A Submersible Stirrers

- YSI 5791A — Submersible Stirrer for field use
- YSI 5795A — Submersible Stirrer for field use
- YSI 5075A — Calibration Chamber for use with field probe
- YSI 5890 — Carrying Case
- YSI 5775 — Membrane and KCl Kit, Standard — includes 2 each 15-membrane packets (.001" thick standard membranes) and a 30 ml bottle KCl with Kodak Photo Flo.
- YSI 5776 — Membrane and KCl Kit, High Sensitivity — includes 2 each 15-membrane packets (.0005" thick membranes) and a 30 ml bottle KCl with Kodak Photo Flo.
- YSI 5945 — "O" Ring Pack — includes (6) "O" rings for each YSI D.O. Probe.
- YSI 5486 — Beator Boot Kit — includes (1) A-05486 Boot, (1) A-05484 Tip, (2) A-05485 Spring. Used only on 5720A and discontinued 5420A and 5720.
- YSI 5986 — Diaphragm Kit for use only with YSI 5739 D.O. Probe.
- YSI 5734 — Adaptor makes it possible to use discontinued YSI 5400 Series Probes with YSI Models 54ARC and 54ABP.
- YSI 5735 — Adaptor makes it possible to use YSI 5739, 5720A and 5750 Probes with discontinued YSI Models 54RC and 54BP.

OXYGEN PROBES AND EQUIPMENT

There are three oxygen probes for use with the YSI Models 54ARC and 54ABP Dissolved Oxygen Meters. Descriptions of where they are used are contained in the following paragraphs.

I. YSI 5739 D.O. Probe

The YSI 5739 probe, with built-in load weight and pressure compensation, is an improved design that replaces the discontinued YSI 5418, 5419, 5718 and 5719 probes. (See Figure 1)

For user convenience the probe is equipped with a disconnecting cable to facilitate changing cable lengths and replacing damaged cables or probes. The probe and cable assembly is held together with a threaded retaining nut. The connection is *not* designed for casual disconnection and should only be disconnected when necessary.

To disconnect the cable unscrew the retaining nut and slide it down the cable to expose the connector. Pull gently on the cable and connector until the connector comes away from the probe body.

To reassemble, inspect the connector and "O" ring for cleanliness. If the "O" ring is frayed or damaged remove it by squeezing it in the groove causing it to bulge, then roll it out of the groove and off the connector. A replacement "O" ring is supplied with the cable.

Push the connector into the probe body, rotating it until the two halves mate. A light coating of vaseline or silicone grease on the "O" ring will make reassembly easier. Air trapped between the connector halves which may cause them to spring apart slightly, is normal. Screw on the retaining nut, *hand tight only*. NOTE: If erratic readings are experienced, disconnect the cable and inspect for water. If present, dry out and reconnect, replacing the "O" ring, if necessary.

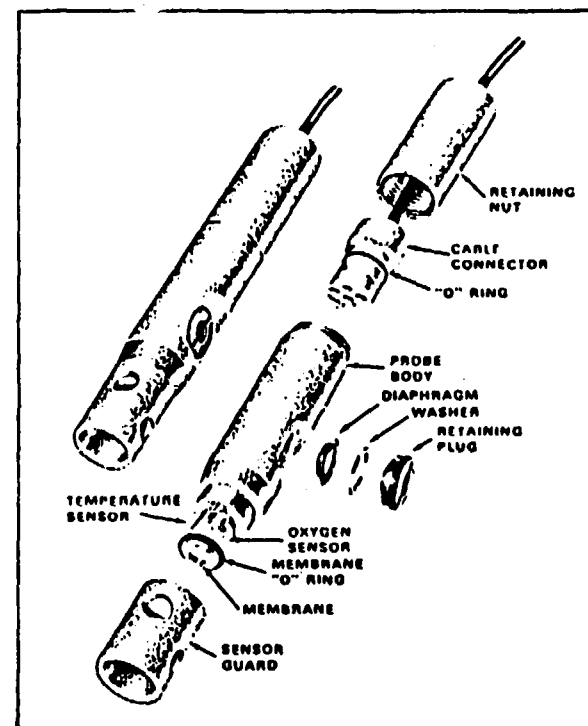


Figure 1

Pressure Compensation

The vent on the side of the probe is part of a unique pressure compensating system that helps assure accurate readings at great depths of water. Pressure compensation is effective to 1/2% of reading with pressures to 100 psi (230 ft. water). The quantity of air bubbles trapped under the membrane determines how serious the pressure error will be, which is why proper preparation of the probe is essential. (See OPERATING PROCEDURES.) The system is designed to accommodate a small amount of trapped air and still function properly, but the amount should be kept to a minimum.

The compensating system normally does not require servicing and should not be taken apart. However, if electrolyte is leaking through the diaphragm or if there is an obvious puncture, the diaphragm must be replaced. A spare is supplied with the probe. Using a coin unscrew the retaining plug and remove the washer and the diaphragm, flush any salt crystals from the reservoir, install the new diaphragm (convolution side in), replace the washer, and screw in the retaining plug.

II. YSI 5720A B.O.D. Bottle Probe

The YSI 5720A B.O.D. Bottle Probe replaces the discontinued YSI 5420A B.O.D. Bottle Probe for measuring dissolved oxygen and temperature in standard B.O.D. bottles. It is provided with an agitator for stirring the sample solution, available in models for 117VAC (95-135VAC, 50-60 Hz) or 230VAC (190-250VAC, 50-60 Hz) operation. (See Figure 2)

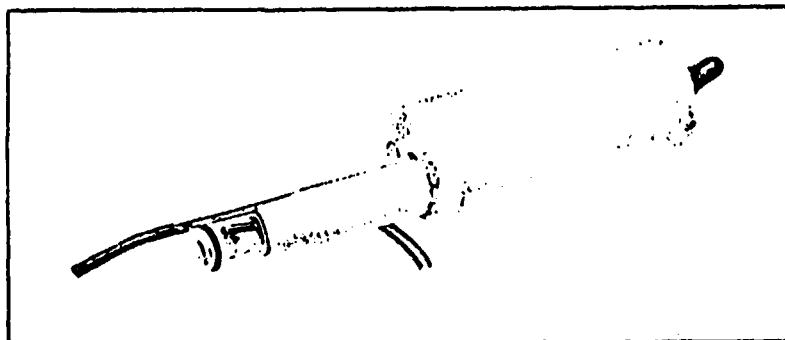


Figure 2

When using the probe, plug the agitator power supply into line power and the probe plug into the instrument. With the agitator turned off place the tapered probe end into the B.O.D. bottle and switch agitator "ON" with switch on top of probe. The probe should be operated with a minimum of trapped air in the B.O.D. bottle. A slight amount of air in the unstirred region at the top of the bottle may be neglected, but no bubbles should be around the thermistor or oxygen sensor.

Stirrer Boot

The probe uses a flexible stirring boot to transmit motion from the sealed motor housing to the sample. If the boot shows signs of cracking or other damage likely to allow leaking into the motor housing, the boot must be replaced.

In fresh water applications boot life is normally several years, but this may be shortened by exposure to hydrocarbons, moderate to strong acids or bases, ozone, or direct sunlight. For maximum life rinse the boot after use in contaminated samples. (See Figure 3)

Boot replacement is as follows:

1. Pull off old assembly and clean shaft.
2. Slide on new assembly making sure the back spring is on the grooved area of the shaft. A small amount of rubber cement may be used.
3. Check that there is sufficient clearance between the tip and the end of the shaft to permit turning without binding.

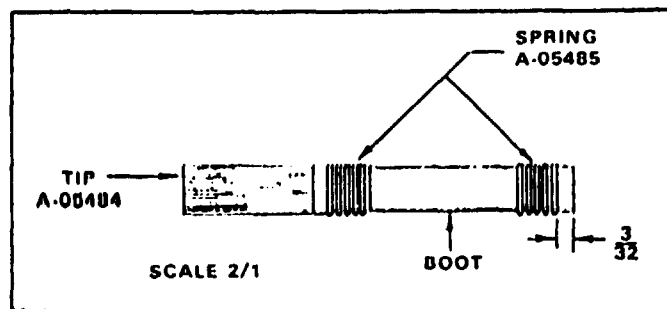


Figure 3

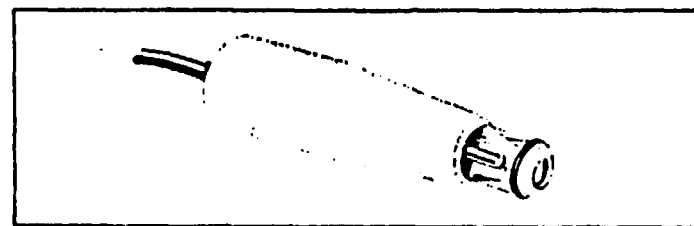


Figure 4

III. YSI 5750 B.O.D. Bottle Probe

The YSI 5750 B.O.D. Bottle Probe replaces the discontinued YSI 5450 B.O.D. Bottle Probe. It is similar to the YSI 5720A B.O.D. Bottle Probe, except that it does not have a stirrer. Agitation of the sample must be provided by other means, such as a magnetic stirrer. (See Figure 4)

IV. Cable Adaptors

All YSI 5700 Series Probes are designed for direct use with the YSI Models 54ARC and 54ABP Dissolved Oxygen Meters. However, to use YSI 5700 probes with the discontinued YSI Models 54RC and 54BP, cable adaptor YSI 5735 is required.

V. YSI 5791A and 5795A Submersible Stirrers

The YSI submersible stirrers are accessories that perform the function of stirring the sample being studied when making dissolved oxygen measurements in the field. The YSI 5791A stirrer can be used with the following dissolved oxygen probes: YSI 5418, 5419, 5718, 5719, and 5739. The YSI 5795A stirrer is only for use with the YSI 5739 Probe. (See Figure 6)

When a stirrer and probe are assembled, the stirrer agitates the sample directly in front of the sensor by means of a rotating eccentric weight which causes the spring-mounted hermetically sealed motor housing to vibrate. An impeller on the end of the motor housing flushes the media across the oxygen sensor. (See sales literature and instruction sheets for further information).

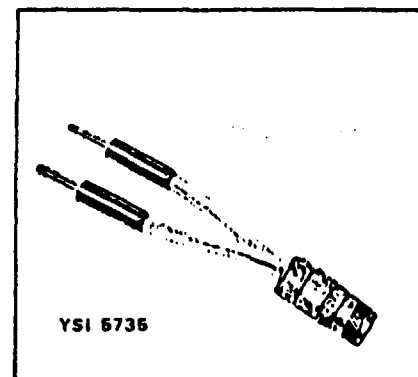


Figure 5

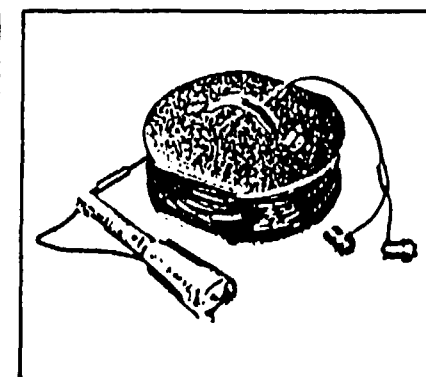


Figure 6

VI. YSI 5492A Battery Pack

The YSI 5492A Battery Pack is designed to attach to the case of all YSI Model 54 Dissolved Oxygen Meters to provide power for operating the submersible stirrers. (See sales literature and instruction sheets for further information).

OPERATING PROCEDURES

1. Preparing the Probe

All YSI 5700 Series Probes have similar sensors and should be cared for in the same manner. They are precision devices relying on good treatment if high accuracy measurements are to be made. Prepare the probes as follows. (See Figure 7)

ALL PROBES ARE SHIPPED DRY — YOU MUST FOLLOW THESE INSTRUCTIONS

1. Prepare the electrolyte by dissolving the KCl crystals in the dropper bottle with distilled water. Fill the bottle to the top.
2. Unscrew the sensor guard from the probe (YSI 5739 only) and then remove the "O" ring and membrane. Thoroughly rinse the sensor with KCl solution.
3. Fill the probe with electrolyte as follows:

A. Grasp the probe in your left hand. When preparing the YSI 5739 probe the pressure compensating vent should be to the right. Successively fill the sensor body with electrolyte while pumping the diaphragm with the eraser end of a pencil or similar soft, blunt tool. Continue filling and pumping until no more air bubbles appear. (With practice you can hold the probe and pump with one hand while filling with the other.) When preparing the YSI 5720A and 5750 probes, simply fill the sensor body until no more air bubbles appear.

B. Secure a membrane under your left thumb. Add more electrolyte to the probe until a large meniscus completely covers the gold cathode. NOTE: Handle membrane material with care, keeping it clean and dust free, touching it only at the ends.

C. With the thumb and forefinger of your other hand, grasp the free end of the membrane.

D. Using a continuous motion stretch the membrane UP, OVER, and DOWN the other side of the sensor. Stretching forms the membrane to the contour of the probe. The membrane can be stretched to approximately 1-1/2 times its normal length.

E. Secure the end of the membrane under the forefinger of the hand holding the probe.

F. Roll the "O" ring over the end of the probe. There should be no wrinkles in the membrane or trapped air bubbles. Some wrinkles may be removed by lightly tugging on the edges of the membrane beyond the "O" ring.

G. Trim off excess membrane with scissors or sharp knife. Check that the stainless steel temperature sensor is not covered by excess membrane.

4. Shake off excess KCl and reinstall the sensor guard.

5. A bottomless plastic bottle is provided with the YSI 5739 probe for convenient storage. Place a small piece of moist towel or sponge in the bottle and insert the probe into the open end. This keeps the electrolyte from dry-

ing out. The YSI 5720A and 5750 probes can be stored in a B.O.D. bottle containing about 1" of water.

6. Membranes will last indefinitely, depending on usage. Average replacement is 2-4 weeks. However, should the electrolyte be allowed to evaporate and an excessive amount of bubbles form under the membrane, or the membrane become damaged, thoroughly flush the reservoir with KCl and install a new membrane.

7. Also replace the membrane if erratic readings are observed or calibration is not stable.

8. "Home brew" electrolyte can be prepared by making a saturated solution of reagent grade KCl and distilled water, and then diluting the solution to half strength with distilled water. Adding two drops of Kodak Photo Flo per 100 ml of solution assures good wetting of the sensor, but is not absolutely essential.

9. The gold cathode should always be bright and untarnished. If it is tarnished (which can result from contact with certain gases) or plated with silver (which can result from extended use with a loose or wrinkled membrane), return it to the factory for service. Never use chemicals or any abrasive.

10. H₂S, SO₂, Halogens, Neon, Nitrous Oxide and CO are interfering gases. If you suspect erroneous readings, it may be necessary to determine if these are the cause. These gases have been tested for response.

100% Carbon Monoxide-Less than 1% 100% Helium-none

100% Carbon Dioxide-Around 1% 100% Nitrous Oxide-1/3 O₂ response

100% Hydrogen-Less than 1% 100% Ethylene-none

100% Chlorine-2/3 O₂ response 100% Nitric Oxide-1/3 O₂ response

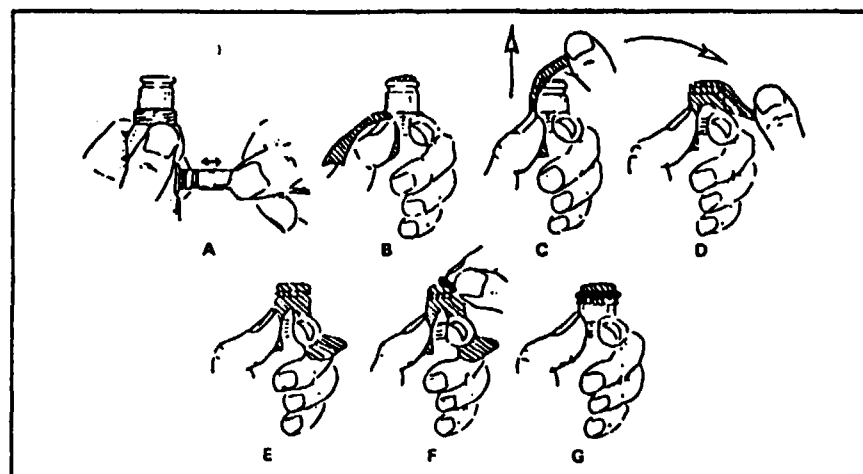


Figure 7

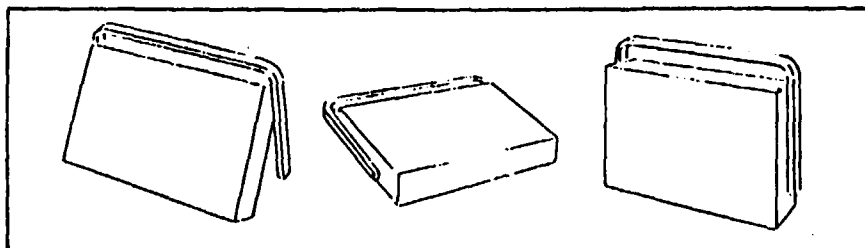


Figure 8

II. Preparing the Instrument

It is important that the instrument be placed in the intended operating position vertical, tilted, or on its back — before it is prepared for use and calibrated. (See Figure 8). Readjustment may be necessary when the instrument operating position is changed. After preparing the probe proceed as follows:

1. With switch in the OFF position, adjust the meter pointer to Zero with the screw in the center of the meter panel. Readjustment may be necessary if the instrument position is changed.
2. Switch to RED LINE and adjust the RED LINE knob until the meter needle aligns with the red mark at the 31°C position.
3. Switch to ZERO and adjust to zero with zero control knob.
4. Attach the prepared probe to the PROBE connector of the instrument and adjust the retaining ring finger tight.
5. Before calibrating allow 15 minutes for optimum probe stabilization. Repolarize whenever the instrument has been OFF or the probe has been disconnected.

III. Calibration

The operator has a choice of three calibration methods — Winkler Titration, Saturated Water, and Air. Experience has shown that air calibration is quite reliable, yet far simpler than the other two methods. The three methods are described in the following paragraphs.

Winkler Titration

1. Draw a volume of water from a common source and carefully divide into four samples. Determine the oxygen in three samples using the Winkler Titration technique and average the three values. If one of the values differs from the other 2 by more than 0.5 mg/l, discard that value and average the remaining two.
2. Place the probe in the fourth sample and stir.
3. Switch to desired mg/l range and adjust the CALIBRATION control to the average value determined in Step 1. Allow the probe to remain in the sample for at least two minutes before setting the calibration value, and leave in the sample for an additional 2 minutes to verify stability. (Readjust if necessary).

Saturated Water

1. Air saturate a volume of water (300-500 cc) by aerating or stirring for at least 15 minutes at a relatively constant temperature.

2. Place the probe in the sample and stir. Switch to TEMPERATURE. Refer to Calibration Table I for the mg/l value corresponding to the temperature.
3. Determine local altitude or the "true" atmospheric pressure (note that "true" atmospheric pressure is as read on a barometer. Weather Bureau reporting of atmospheric pressure is corrected to sea level). Using Calibration Table II determine the correction factor for your pressure or altitude.

4. Multiply the mg/l value from Table I by the correction factor from Table II to determine the corrected calibration value for your conditions.

EXAMPLE: Assume temperature = 21°C and altitude = 1000 feet. From Table I the calibration value for 21°C is 8.9 mg/l. From Table II the correction factor for 1000 feet is about 0.96. The corrected calibration value is $8.9 \text{ mg/l} \times 0.96 = 8.54 \text{ mg/l}$.

5. Switch to an appropriate mg/l range and adjust the CALIBRATE knob while stirring until the meter reads the corrected calibration value from Step 4. Leave the probe in the sample for two minutes to verify calibration stability. Readjust if necessary.

Air Calibration — Fresh Water

1. Place the probe in moist air. B.O.D. probes can be placed in partially filled (50 ml) B.O.D. bottles. Other probes can be placed in the YSI 5075A Calibration Chamber (refer to the following section describing CALIBRATION CHAMBER) or the small calibration bottle (the one with the hole in the bottom) along with a few drops of water. The probe can also be wrapped loosely in a damp cloth taking care the cloth does not touch the membrane. Wait approximately 10 minutes for temperature stabilization. This may be done simultaneously while the probe is stabilizing.
2. Switch to TEMPERATURE and read. Refer to Table I — Solubility of Oxygen in Fresh Water, and determine calibration value.
3. Determine altitude or atmospheric correction factor using Table II.
4. Multiply the calibration value from Table I by the correction factor from Table II.

EXAMPLE: Assume temperature = 21°C and altitude = 1000 feet. From Table I the calibration value for 21°C is 8.9 mg/l. From Table II the correction factor for 1000 feet is about 0.96. Therefore, the corrected calibration value is $8.9 \text{ mg/l} \times 0.96 = 8.54 \text{ mg/l}$.

5. Switch to the appropriate mg/l range and adjust the CALIBRATE knob until the meter reads the corrected calibration value from Step 4. Wait two minutes to verify calibration stability.

Readjust if necessary.

Air Calibration — Sea Water

1. Place the probe in moist air. B.O.D. probes can be placed in partially filled (50 ml) B.O.D. bottles. Other probes can be placed in the YSI 5075A Calibration Chamber (refer to the following section describing Calibration Chamber) or the small storage bottle (the one with the hole in the bottom) along with a few drops of water. The probe can also be wrapped loosely in a damp cloth taking care the cloth does not touch the membrane. Wait approximately 10 minutes for temperature stabilization. This may be done simultaneously while the probe is polarizing.

2. Switch to TEMPERATURE and read. Refer to Table III — Solubility of Oxygen in Sea Water, and determine calibration value.
3. Switch to the appropriate mg/l range, and adjust the CALIBRATE knob until the meter reads the calibration value determined in Step 2. Wait 2 minutes to verify calibration stability. Readjust if necessary.

The probe is now calibrated and should hold this calibration value for many measurements. Calibration can be disturbed by physical shock, touching the membrane, or drying out of the electrolyte. Check calibration after each series of measurements and in time you will develop a realistic schedule for recalibration. For best results when not in use, follow the storage procedures recommended for the various probes described under OXYGEN PROBES AND EQUIPMENT. This will reduce drying out and the need to change membranes.

Calibration Chamber

The YSI 5075A Calibration Chamber is an accessory that helps obtain optimum calibration in the field and is also a useful tool for measuring at shallow depths (less than 4').

As shown in Figure (A), it consists of a 4-1/2 foot stainless steel tube (1) attached to the calibration chamber (2), the measuring ring (3), and two stoppers (4) and (5).

For calibration, insert the solid stopper (4) in the bottom of the calibration chamber (2). Push the oxygen probe (6) through the hollow stopper (5) as shown in Figure (B). Place the probe in the measuring ring, Figure (C), and immerse the probe in the sample to be measured for five minutes to thermally equilibrate the probe. Quickly transfer the probe to the calibration chamber (5) draining excess water from the chamber and shaking any excess droplets from

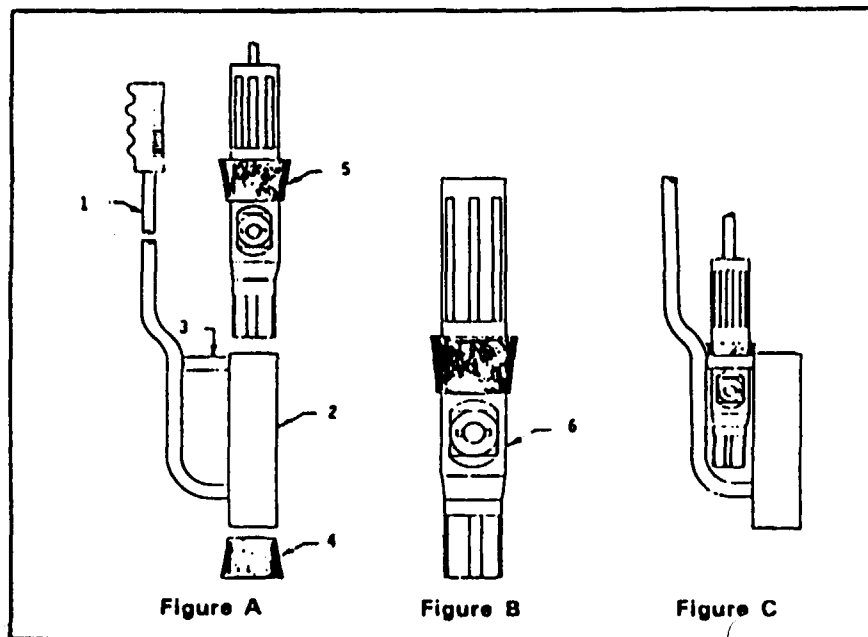


Figure 9

the probe membrane. For maximum accuracy, wet the inside of the calibration chamber with fresh water. This creates a 100% relative humidity environment for calibration. Place the chamber in the sample for an additional five minutes for final thermal equilibrium. Calibrate the probe as described in the air-calibration procedure. Keep the handle above water at all times.

After calibration, return the probe to the measurement ring for shallow measurements. Move the probe up and down, or horizontally, approximately one foot a second while measuring. In rapidly flowing streams (greater than 5'/second) install the probe in the measuring ring with the pressure compensating diaphragm towards the chamber.

IV. Dissolved Oxygen Measurement

With the instrument prepared for use and the probe calibrated, place the probe in the sample to be measured and provide stirring.

1. Stirring for the YSI 6739 Probe can best be accomplished with a YSI submersible stirrer. If the submersible stirrer is not used, provide manual stirring by raising and lowering the probe about 1 ft. per second. If the 5075 Calibration Chamber is used, the entire chamber may be moved up and down in the water at about 1 ft. per second.
2. The YSI 5720A has a built-in power driven stirrer.
3. With the YSI 5750 sample stirring must be accomplished by other means such as with the use of a magnetic stirring bar.
4. Allow sufficient time for probe to stabilize to sample temperature and dissolved oxygen.
5. Read dissolved oxygen.

V. High Sensitivity Membrane

Use of high sensitivity .0005" membranes (YSI 5776) in place of standard .001" membrane (YSI 5775) is recommended when measurements are to be made consistently at low temperatures (less than 15°C). Calibration and readings will be made just as if the standard YSI 5775 Membrane was being used.

The YSI 5776 High Sensitivity Membranes can also be used in certain situations to increase sensitivity at temperatures about 15°C. The ranges thus become 0-5 and 0-10 mg/l. When calibration with high sensitivity membranes is attempted at temperatures greater than 15°C the selector switch must be set to 0-20 mg/l. Multiply the calculated calibration value by 2. For example: at 21°C and 1000 ft. altitude the calibration value would be 8.6 x 2 or 17.2. Remember the 0-10 and 0-20 mg/l ranges are now 0-5 and 0-10 mg/l, and all mg/l readings must be divided by 2 for a final reading. When operating in this manner accuracy will be degraded slightly.

VI. Recorder Output

Red and black recorder jacks are provided on the YSI Models 54ARC and 54ABP, if you wish to record data while measuring. The high terminal of the recorder is connected to the red tip jack and the low terminal to the black. Output of the YSI 54A at full scale is between 114 to 136 mV.

Use a 50K or higher input impedance recorder and operate it with the terminals ungrounded. The recorder should be operated with its terminals ungrounded. Calibration of the instrument should be checked after connection of

Many recorders have an adjustable full scale sensitivity feature. When these recorders are used with the Model 54A, use the 100 millivolt range and adjust the full scale chart deflection when there is full scale motor deflection. Refer to the instruction book for the recorder. For recorders without this feature, a simple divider network as shown below can be constructed. This is adequate to adjust the signal for full scale chart and motor deflection on the 100 mV fixed range recorders.

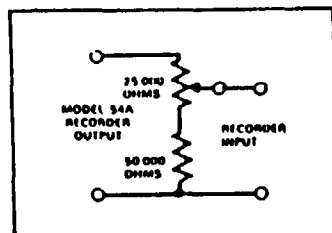


Figure 10

VIII. Calibration Tables

Table I shows the amount of oxygen in mg/l that is dissolved in air saturated fresh water at sea level (760 mmHg atmospheric pressure) as temperature varies from 0° to 45°C.

Table I — Solubility of Oxygen in Fresh Water

Temperature °C	mg/l Dissolved Oxygen	Temperature °C	mg/l Dissolved Oxygen
0	14.60	23	8.56
1	14.19	24	8.40
2	13.81	25	8.24
3	13.44	26	8.09
4	13.09	27	7.95
5	12.75	28	7.81
6	12.43	29	7.67
7	12.12	30	7.54
8	11.83	31	7.41
9	11.55	32	7.28
10	11.27	33	7.16
11	11.01	34	7.05
12	10.76	35	6.93
13	10.52	36	6.82
14	10.29	37	6.71
15	10.07	38	6.61
16	9.85	39	6.51
17	9.65	40	6.41
18	9.45	41	6.31
19	9.26	42	6.22
20	9.07	43	6.13
21	8.90	44	6.04
22	8.72	45	5.95

Source: Derived from 15th Edition "Standard Methods for the Examination of Water and Wastewater."

Table II — Correction for Atmospheric Pressure

Table II shows the correction factor that should be used to correct the calibration value for the effects of atmospheric pressure or altitude. Find true atmospheric pressure in the left hand column and read across to the right hand column to determine the correction factor. (Note that "true" atmospheric pressure is as read on a barometer. Weather Bureau reporting of atmospheric pressure is corrected to sea level.) If atmospheric pressure is unknown, the local altitude may be substituted. Select the altitude in the center column and read across to the right hand column for the correction factor.

Table II

Atmospheric Pressure mmHg	or Equivalent Altitude Ft.	= Correction Factor
775	540	1.02
760	0	1.00
745	542	.98
730	1094	.96
714	1688	.94
699	2274	.92
684	2864	.90
669	3400	.88
654	4082	.86
638	4756	.84
623	5403	.82
608	6065	.80
593	6744	.78
578	7440	.76
562	8204	.74
547	8939	.72
532	9694	.70
517	10472	.68
502	11273	.66

Source: Derived from 15th Edition "Standard Materials for the Examination of Water and Wastewater."

The temperature-solubility relationship of oxygen in sea water is not the same as that in fresh water. For this reason the compensation error when used with sea water is greater than when used with fresh water. For a $\pm 5^{\circ}\text{C}$ span the error could be +2.2% of reading and over the temperature range of -2° to $+30^{\circ}\text{C}$ the error could be 6.3% of reading.

Table III — Solubility of Oxygen in Sea Water

SOLUBILITY OF OXYGEN IN SEA WATER
(Chloride concentration 20,000 mg/l)

Temp. °C	Solubility mg/l	Temp. °C	Solubility mg/l
0	11.41	16	7.91
1	11.11	17	7.78
2	10.83	18	7.61
3	10.56	19	7.47
4	10.30	20	7.33
5	10.05	21	7.20
6	9.82	22	7.07
7	9.59	23	6.95
8	9.37	24	6.83
9	9.16	25	6.71
10	8.96	26	6.60
11	8.77	27	6.49
12	8.58	28	6.38
13	8.41	29	6.28
14	8.24	30	6.18
15	8.07		

Source: Derived from 15th Edition "Standard Materials for the Examination of Water and Wastewater."

Correcting for Salinity

When measuring dissolved oxygen in water samples with a salinity or chlorinity between sea water and fresh water, calibrate the instrument for fresh water and make your measurements. Then correct the data according to the following formula:

FORMULA:

$$A = M \left[1.0 - \left(\frac{Cs/Co [Sf \cdot So]}{Sf} \right) \right]$$

Where: A = Actual DO of sample, (mg/l dissolved O_2)

M = Measured DO with instrument

Co = Chlorinity of ocean water (20 o/oo Cl ion)

Cs = Chlorinity of sample (o/oo Cl ion)

Sf = DO of saturated fresh water at 760 mm pressure and at same temperature as sample (mg/l DO, obtain data from charts in instruction manual)

So = DO of saturated ocean water (20,000 mg/l Chloride ion) at 760 mm pressure and at same temperature as sample (mg/l DO, obtain data from instruction manual)

* NOTE: If salinity is used instead of chlorinity the ratio Cs/Co is computed using 36.11 o/oo for Co (salinity of ocean water), and the salinity of your sample of Cs.

EXAMPLE: Measured Data

DO = 4.1

Temp = 22°C

Salinity = 31 o/oo salinity

M = 4.1 mg/l DO from data

Co = 36.11 o/oo salinity from manual

Cs = 31.0 o/oo salinity from data

Sf = 8.8 mg/l DO from Table I in manual

So = 7.1 mg/l DO from Table II in manual

$$\begin{aligned} A &= 4.1 \left[1.0 - \left(\frac{[31.0/36.11] [8.8 - 7.1]}{8.8} \right) \right] \\ &= 4.1 \left[1.0 - \left(\frac{[.86] [1.7]}{8.8} \right) \right] \\ &= \frac{(1.46)}{8.8} \\ &= 4.1 [1.0 - (.88)] \\ &= 4.1 [1.0 - 0.166] \\ &= 4.1 [0.834] \\ &= 3.41 \text{ mg/l} \end{aligned}$$

DISCUSSION OF MEASUREMENT ERRORS

There are three basic types of errors which can occur. Type I errors are related to limitations of the instrument design and tolerances of the instrument components. These are chiefly the meter linearity and resistor tolerances. Type II errors are due to basic probe accuracy tolerances, chiefly background signal, probe linearity, and variations in membrane temperature coefficient. Type III errors are related to the operator's ability to determine the conditions at the time of calibration. If calibration is performed against more accurately known conditions, Type III errors are appropriately reduced.

Individual Sources of Error

This description of sources of error can be used to attach a confidence to any particular reading of dissolved oxygen. The particular example given is for a near extreme set of conditions. As a generality, overall error is diminished when the probe and instrument are calibrated under conditions of temperature and dissolved oxygen which closely match the sample temperature and dissolved oxygen.

Type I

A — is the error due to meter linearity

Error = +1% full scale of the measurement range.

B — is the error due to tolerances in the instrument when transferring a reading from one range to another. Error = $\pm 1\%$ of the reading.

Type II

A — errors due to probe background current

Error = $1.0\% \left(1 - \left(\frac{\text{Meter Reading mg/l}}{\text{Calibration Value mg/l}} \right) \right) \times \text{Calib. Value, mg/l}$

B — errors due to probe non-linearity. Error = $\pm 0.3\%$ of reading.

C — error caused by variability in the probe membrane temperature coefficient.

Error = zero if readings are taken at the calibration temperature

Error = $\pm 1\%$ of meter reading if readings are taken within 5°C of the calibration temperature.

Error = $\pm 3\%$ of meter reading for all other conditions.

Type III

A — errors due to the accuracy of the instrument thermometer when used to measure the exact probe temperature during calibration.

Error = $\pm 1.5\%$ of reading.

B — errors due to the assumption of mean barometric pressure.

Daily variation is usually less than 1.7% .

Error = $\pm 1.7\%$ of reading.

C — errors assume an ability to estimate altitude to within ± 500 ft. when computing the altitude correction factor.

Error = $\pm 1.8\%$ of reading.

D — errors consider the possibility of only 50% relative humidity when calibrating the probe. If the actual relative humidity is 50% instead of 100% , the errors will be as follows:

Calibration Temperature \pm C	Error in percent of reading
0	(-) 0.3
10	(-) 0.6
20	(-) 1.15
30	(-) 2.11
40	(-) 3.60

Example of a Typical Error Calculation

The example given presumes the air calibration technique. If calibration is done with air saturated water, the relative humidity consideration (III-D) is eliminated. If the Winkler calibration method is used, Type III errors are deleted and replaced by the uncertainty attributable to the overall Winkler determination.

Data: Instrument calibrated at 25°C , elevation estimated at $2000' \pm 500'$, normal barometric pressure assumed, calibrated on $0-10$ mg/l range at 7.8 mg/l, readings taken on $0-20$ mg/l range at 10.5 mg/l at 8°C .

Type	Description	Calculations	Error mg/l
IA	Linearity	$= .01 \times 10.5 \text{ mg/l}$	$= .10$
IB	Range Change	$= .01 \times 10.5 \text{ mg/l}$	$= .10$
IIA	Probe Background	$= .01 \times \left(1 - \frac{10.5}{7.8} \right) 7.8 \text{ mg/l}$	$= .03$
IIB	Probe Linearity	$= .003 \times 10.5 \text{ mg/l}$	$= .03$
IIC	Temp. Compensation	$= .03 \times 10.5 \text{ mg/l}$	$= .31$
IIIA	Temp. Measurement	$= .015 \times 10.5 \text{ mg/l}$	$= .16$
IIIB	Pressure	$= .017 \times 10.5 \text{ mg/l}$	$= .18$
IIIC	Altitude	$= .18 \times 10.5 \text{ mg/l}$	$= .19$
IIID	R.H.	$= .016 \times 10.5 \text{ mg/l}$	$= .17$
Maximum Possible Error			$= 1.27 \text{ mg/l}$
Probable Error			$= \pm .63 \text{ mg/l}$

Considering a statistical treatment of the probable error at any time for any instrument, it is likely that the actual error in any measurement will be about $1/2$ of the possible error. In this case the probable error is about $\pm .5$ mg/l out of a reading of 10.5 mg/l, or 4.8% of the reading.

INSTRUMENT BATTERIES

Battery replacement or recharging on the YSI Model 54A is indicated if the "red line" adjustment cannot be made or O_2 calibration cannot be achieved. (Warning: a faulty probe will also not permit O_2 calibration.)

To replace batteries remove the four screws holding the rear cover of the instrument. The four batteries will be found on the battery terminal board inside. CAUTION: disconnect battery charger on YSI Model 54ARC before removing cover.

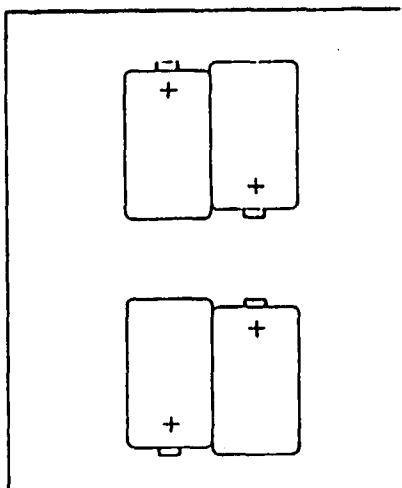


Figure 11

The YSI Model 54ARC contains four 1.25V Ni-Cd batteries (Burgess CD6 or equivalent). (See Figure 11). These batteries should be recharged when the instrument can no longer be red lined. Battery life should be three years or longer. Deeper discharge because of longer intervals between recharge will result in shorter battery life. The batteries should be recharged overnight, about 16 hours with the instrument off or 20 hours with the YSI Model 54ARC turned on.

The YSI Model 54ABP contains four 1.5V carbon-zinc (Panasonic UM-2N or equivalent). The life of these batteries is 1000 hours. Replace batteries every six months to minimize danger of corrosion due to dead or leaky batteries.

Battery holders are color coded. Positive (+ button) end of battery must go to red. (See Figure 11).

WARRANTY AND REPAIR

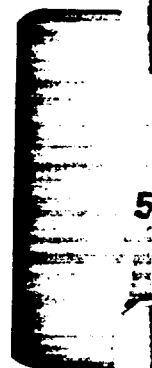
All YSI products carry a one-year warranty on workmanship and parts exclusive of batteries. Damage through accident, misuse, or tampering will be repaired at a nominal charge, if possible, when the item is returned to the factory or to an authorized YSI dealer.

If you are experiencing difficulty with any YSI product, it may be returned for repair, even if the warranty has expired. YSI maintains complete facilities for prompt servicing for all YSI products.

YELLOW SPRINGS INSTRUMENT CO., INC.
SERVICE DEPARTMENT
P.O. BOX 279
YELLOW SPRINGS, OHIO 45387, U.S.A.
PHONE: 513-767-7241

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APPENDIX B-5
REDUCTION/OXIDATION POTENTIAL ANALYSIS
OF GROUNDWATER

FIELD MEASUREMENT OF OXIDATION-REDUCTION POTENTIAL

Method: Electrometric
Reference: Beckman Instruments, 1987
Sensitivity: 1 mV
Optimum Range: -999.9 mV to +999.9 mV
Sample Handling: Determine on-site or within 4 hours

Reagents and Apparatus:

1. pH meter in absolute millivolt mode
2. Platinum combination electrodes
3. Beakers or plastic cups
4. pH buffer solutions, pH 4 and 7 saturated with a few crystals of quinhydrone
5. Deionized water in squirt bottle
6. All glassware soap and water washed, followed by two hot water rinses and two deionized water rinses.

Calibration:

1. Short the meter glass and reference inputs and adjust the STANDARDIZE control until zero millivolts is displayed.
2. Place electrode in pH 4 buffer solution saturated with quinhydrone.
3. Record mV reading and compare to chart on Table 1.
4. Rinse electrode with deionized water and place in pH 7 buffer solution saturated with quinhydrone.
5. Record mV reading and compare to chart on Table 1.
6. If mV readings do not agree within ± 10 mV of the Table 1 values at the given temperature, follow electrode maintenance procedures described in the attached manual and recalibrate.

Procedure:

1. Calibrate meter using calibration procedure.
2. Pour the sample into a clean beaker or plastic cup.
3. Immerse electrode in solution allowing several minutes for meter to stabilize. Make sure the white AgCl junction on side of electrode is in the solution. The level of electrode solution must be approximately one inch above sample to be measured.
4. Rinse electrode with deionized water between samples. Recheck calibration with pH 4 buffer solution saturated with quinhydrone after every 5 samples.

Notes:

1. Eh is temperature and pH dependent. Therefore, the temperature and pH of samples should be measured at the same time as redox. For refrigerated or cool samples, use refrigerated buffers to calibrate meter.
2. Weak organic and inorganic salts and oil and grease are interferences in Eh measurements. If oil and grease are visible, note on data sheet. Clean electrode with soap and water, polish with scouring powder and rinse with distilled water. Then recalibrate meter.
3. Before going into the field:
 - a. Check batteries;
 - b. Do a quick calibration with quinhydrone saturated pH 7 buffer solution to check electrode;
 - c. Prepare fresh quinhydrone saturated pH 4 and pH 7 solutions daily.
4. Following field measurements:
 - a. Report any problems;
 - b. Compare with previous data;
 - c. Clean all dirt off of meter and inside case;
 - d. Store electrode as follows:
 1. Slide rubber sleeve into position over the filling hole.
 2. Place cot over tip of electrode by threading platinum wire through opening and sliding cot onto glass body until porous plug is completely covered.

Table 1

Redox Potential Calibration Chart

Quinhydrone Saturated pH 4 Solution

Temperature °C	20°	25°	30°
Theoretical Value (mV)	+268 mV	+263 mV	+258 mV

Quinhydrone Saturated pH 7 Solution

Temperature °C	20°	25°	30°
Theoretical Value (mV)	+92 mV	+86 mV	+79 mV

Instrument reading should be within ± 10 mV of Theoretical

[wpmisc-400-12]

BECKMAN

Φ 10 pH Meter

Φ 11 pH Meter

Φ 12 pH/SE Meter

ASCC.

WARRANTY

Your Φ^{TM} (pHTM) 10, 11, or 12 pH Meter is warranted to be free of manufacturing defects for one (1) year from the date of purchase. This does not include any defects that are the result of abuse or misuse of the instrument. Beckman Instruments, Inc., will, at Beckman's option, repair or replace your instrument with a comparable unit. This is a limited warranty. You may have additional rights under your state laws. Batteries are not included in this warranty.

WARNING: This equipment generates, uses, and can radiate radio frequency energy and may cause interference to radio communications. Improper installation or modification of the equipment may increase interference. It has been tested and found to comply with the limits for a Class A computing device pursuant to Subpart J of Part 15 of FCC Rules, which are designed to provide reasonable protection against such interference when operated in a commercial environment.

Operation of this equipment in a residential area may cause interference, in which case the user at his own expense will be required to take whatever measures may be required to correct the interference.

Beckman Instructions 015-246800-8

BECKMAN

Φ^{TM} 10 pH Meter

Φ^{TM} 11 pH Meter

Φ^{TM} 12 pH/ISE Meter

pH MEASUREMENT (Two-standard method: Condensed instructions)

I. SETUP

① Prepare buffers (eg., pH 4 and 7).	② Prepare sample.	③ Prepare deionized or distilled water for electrode rinse.
④ Connect electrodes to instrument. (1) Omit reference if combination electrode is used. (2) ATC optional.	⑤ Turn on and clear instrument.	⑥ Display will read:

II. STANDARDIZE

① Rinse electrode(s). Blot excess.	② Immerse electrode(s) in STD.1. Stir briefly.	③ Press pH , then STD 1 .	④ After STD stops flashing, display will read pH of STD.1
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⑤ Rinse electrode(s). Blot excess.	⑥ Immerse electrode(s) in STD 2. Stir briefly.	⑦ Press STD 2 .	⑧ After STD stops flashing, display will read pH of STD 2.
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III. MEASURE pH

① Rinse electrode(s). Blot excess.	② Immerse electrode(s) in sample. Stir briefly.	③ Press pH .	④ After STD stops flashing, display will read pH of sample.
---------------------------------------	--	------------------------	---

FOR MORE DETAILED INSTRUCTIONS ON pH MEASUREMENT, SEE NEXT PAGE.

MEASURING mV AND RELATIVE mV (Φ11, Φ12)

MEASURING CONCENTRATION (Φ12)

INSTRUMENT FUNCTIONS AND FEATURES

ELECTRODES, BUFFERS, AND ACCESSORIES

BATTERY REPLACEMENT, SERVICE
AND TROUBLESHOOTING

SPECIFICATIONS

pH MEASUREMENT: DETAILED INSTRUCTIONS

METHODS: The pH1 10, 11, and 12 can measure pH from 0 to 15.99. They will perform one- or two-point standardization automatically, using any buffer listed below, at any temperature between -5°C and 100°C.

STANDARD pH BUFFERS RECOGNIZED BY THE pH1 10, 11, AND 12:

1.68, 4.00, 7.00, 10.01, 12.45.

TWO-POINT STANDARDIZATION METHOD:

Two-point standardization, the preferred and more accurate method of pH measurement, should be used when pH accuracy of beyond ± 0.1 pH is required. Use buffers as close to the sample pH as possible, one above, and one below. (For example, if sample pH is about 8.5, use 7.00 and 10.01 pH buffers).

ONE-POINT STANDARDIZATION METHOD:

One-point standardization, a somewhat faster procedure, is recommended only if (a), accuracy of ± 0.1 pH unit is acceptable, and (b), sample pH is within 1.5 pH of that of the buffer used for standardization.

pH MEASUREMENT PROCEDURE:

1. Connect electrode(s) to appropriate input(s):
 - a. If a combination electrode is used, connect it to the input marked "pH".
 - b. If an electrode pair is used, connect the indicating electrode to the input marked "pH" and the reference electrode to the input marked "REF".
 - c. For better accuracy, or when measuring and/or standardizing at a temperature other than 25°C, connect a Beckman 598115 Automatic Temperature Compensator probe to input marked "ATC".
2. Press **[ON]** to turn on instrument, then press **[C]** to clear. Display will show (Ck, AUTO).
3. Rinse electrode(s) (and ATC if used) with deionized water. Blot excess.
4. Immerse electrode(s) (and ATC if used) in first standard. Stir briefly with electrodes to remove bubbles from electrode surfaces. Press **[M]**. Displayed pH value will have a resolution of 0.01. If 0.1 resolution is desired, press **[H]**.
5. Press **[H]**. When **[CD]** stops flashing, display will show [pH value locked, **CD**, **►** m].
6. Rinse electrode(s) (and ATC probe if used) with deionized water. Blot excess. Proceed to appropriate step, according to desired type of standardization:
 - a. If ONE-POINT standardization is to be used, instrument is ready for sample measurement; proceed to Step 9.
 - b. If TWO-POINT standardization is desired, proceed to Step 7.
7. Immerse electrode(s) (and ATC if used) in second standard. Stir briefly with electrodes to remove bubbles from electrode surfaces. Press **[M]**. When **[CD]** stops flashing, display will show [pH value locked, **CD**, **►** m, **►** m].
8. Rinse electrode(s), (and ATC probe if used) with deionized water. Blot excess.
9. Immerse electrode(s) (and ATC if used) in sample. Stir briefly with electrodes. Press **[M]**. When **[CD]** stops flashing, display will show [pH value locked, **CD**]. Measurement is now complete. Repeat Steps 6 and 9, above, for additional samples.
10. If continuous pH monitoring is desired, press **[RM]** to turn off Auto Read function.

MEASURING mV AND RELATIVE mV (Φ11, Φ12)

MEASURING CONCENTRATION (Φ12)

INSTRUMENT FUNCTIONS AND FEATURES

ELECTRODES, BUFFERS, AND ACCESSORIES

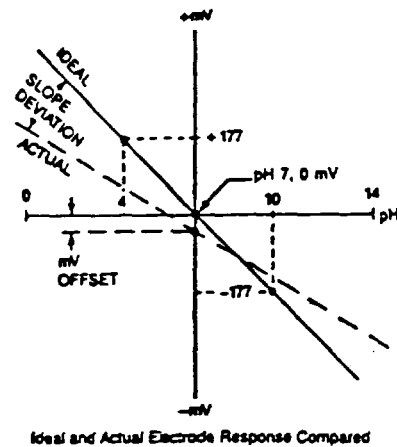
BATTERY REPLACEMENT, SERVICE AND TROUBLESHOOTING

SPECIFICATIONS

pH MEASUREMENT: PRINCIPLES AND THEORY

The pH 10/11/12 pH Meter is essentially a high-impedance voltmeter with a microcomputer that translates voltage and temperature data into pH units. At 25°C, the ideal pH electrode system develops -59 mV per pH unit increase, with 7.00 pH = 0 mV.

Standardization allows the meter to compensate for non-ideal electrode characteristics. One-point standardization compensates for millivolt offset; two-point standardization compensates for both millivolt offset and slope deviation. See diagram below.



The pH 10, 11, and 12 may be standardized with any of five standard pH buffers: 1.68, 4.00, 7.00, 10.01, and 12.45. Standardization may be accomplished with any two buffers, used in any order (and at any temperature, if ATC is used). When $\left(\frac{pH}{mV}\right)$ is pressed, the instrument automatically recognizes the buffer.

The relationship between pH and electrode voltage changes with temperature. For precise pH measurements or temperatures not close to 25°C, a Beckman 598115 ATC (Automatic Temperature Compensator) probe should be used. With this probe, the instrument automatically compensates for the temperature characteristics of the buffer, permitting a sample to be measured at any temperature, even if different from the buffer temperatures. With ATC, the instrument measures and displays temperatures from -5°C to 100°C.

If an ATC probe is not used, the instrument defaults and displays 25°C.

The pH calculation is based on the Nernst equation:

$$E = E_0 - \frac{2.3 RT}{nF} \log a_i$$

E is the total potential, in millivolts, developed between the sensing and reference electrodes; E_0 varies with the choice of electrodes, temperature, and pressure; $2.3RT/nF$ is the Nernst factor (R and F are constants, n is the charge on the ion, including sign, T is the temperature in degrees Kelvin), and a_i is the activity of the ion to which the electrode is responding.

For further information on principles and theory of pH measurement, refer to The Beckman Handbook of Applied Electrochemistry (Beckman Bulletin 7739).

MEASURING mV AND RELATIVE mV (Φ11, Φ12)

MEASURING CONCENTRATION (Φ12)



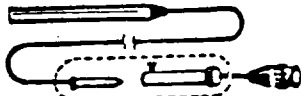


INSTRUMENT FUNCTIONS AND FEATURES


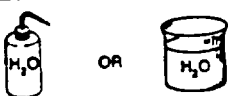


ELECTRODES, BUFFERS, AND ACCESSORIES

**BATTERY REPLACEMENT, SERVICE
AND TROUBLESHOOTING**

SPECIFICATIONS

FOR ACCURATE mV MEASUREMENTS WITH THE $\Phi 11$ OR $\Phi 12$, THE FOLLOWING ITEMS ARE RECOMMENDED:

1.		pH indicating electrode, Futura II. Futura II cable with BNC connector. NOTE: If combination pH electrode is used, omit separate reference electrode (item 2, below).
OR		
1a.		Metallic electrode with 2 mm pin connector + pin-to-BNC adapter.
OR		
1b.		Ion-Selective electrode with BNC connector (or U.S. standard connector + U.S. standard-to-BNC adapter).
2.		Reference electrode, Futura II. Cable with 2 mm pin connector, Futura II. NOTE: Omit reference electrode if combination pH electrode is used.
3.		Standard solution(s); appropriate to the application.

4.		Clean beaker(s) or equivalent container(s), 100-250 mL, for containing standard solution(s).
5.		Squirt bottle or beaker containing deionized or distilled water for rinsing electrodes.
6.		Clean towels, "Kimwipes", etc., for blotting electrodes.
7.		The sample to be measured.

For part numbers, see "Electrodes, Buffers, and Accessories."
For mV measurement procedures, see next page.

MEASURING mV AND RELATIVE mV ($\Phi 11$, $\Phi 12$)

MEASURING CONCENTRATION ($\Phi 12$)

INSTRUMENT FUNCTIONS AND FEATURES



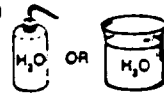
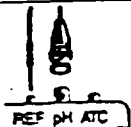
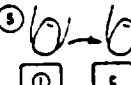
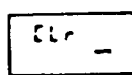
ELECTRODES, BUFFERS, AND ACCESSORIES

BATTERY REPLACEMENT, SERVICE
AND TROUBLESHOOTING




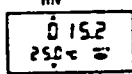
SPECIFICATIONS

mV MEASUREMENT: CONDENSED INSTRUCTIONS




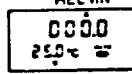



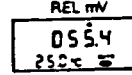
I. SETUP

<p>①</p>  <p>STANDARD</p> <p>Prepare standard solution.</p>	<p>②</p>  <p>SAMPLE</p> <p>Prepare sample.</p>	<p>③</p>  <p>H₂O OR H₂O</p> <p>Prepare deionized or distilled water for electrode rinse.</p>
<p>④</p>  <p>REF pH ATC</p> <p>Connect electrodes to instrument.</p>	<p>⑤</p>  <p>Turn on and clear instrument.</p>	<p>⑥</p> <p>Display will read:</p> 

II. mV MEASUREMENT, ABSOLUTE. FOR RELATIVE mV MEASUREMENT, SEE III, BELOW.

<p>①</p>  <p>H₂O</p> <p>Rinse electrode(s). Blot excess H₂O.</p>	<p>②</p>  <p>STANDARD OR SAMPLE</p> <p>Immerse electrode(s) in standard or sample. Stir briefly.</p>	<p>③</p>  <p>Press mV.</p>	<p>④</p> <p>After mV stops flashing, display will read absolute mV of solution. mV</p> 
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For RELATIVE mV Measurement,
Proceed with following steps:

<h3>III. mV MEASUREMENT, RELATIVE</h3>			
<p>①</p>  <p>H₂O</p> <p>Rinse Electrodes. Blot excess.</p>	<p>②</p>  <p>STANDARD</p> <p>Immerse electrodes in standard solution to be used to establish zero mV point. Stir briefly.</p>	<p>③</p>  <p>Press mV then STD.</p>	<p>④</p> <p>After mV stops flashing, display will read 000.0 mV REL mV</p> 
<p>⑤</p>  <p>H₂O</p> <p>Rinse electrodes. Blot excess.</p>	<p>⑥</p>  <p>SAMPLE</p> <p>Immerse electrodes in sample. Stir briefly.</p>	<p>⑦</p>  <p>Press mV.</p>	<p>⑧</p> <p>After mV stops flashing, display will read mV relative to the standard. REL mV</p> 

NOTE
INSTRUMENT WILL REMAIN IN RELATIVE mV MODE UNTIL
EITHER **μ**, **CONC**, OR **°C** IS PRESSED.

FOR MORE DETAILED INSTRUCTIONS ON mV MEASUREMENT, PROCEED TO NEXT PAGE.

MEASURING CONCENTRATION (Φ12)

INSTRUMENT FUNCTIONS AND FEATURES

ELECTRODES, BUFFERS, AND ACCESSORIES

BATTERY REPLACEMENT, SERVICE
AND TROUBLESHOOTING

mV MEASUREMENT: DETAILED INSTRUCTIONS

mV MEASUREMENT: TYPICAL USES

Some uses of the mV mode are monitoring chemical reactions, quantifying ions, and determining the oxidizing-reducing potential (ORP) of a given sample. Because such measurements are usually not specific for a particular ion or species, readings must be interpreted carefully to obtain meaningful results. The user should have an understanding of the reaction that is occurring, or is desired, and of any sample components that could potentially interfere. For more detailed information, refer to the Beckman Handbook of Applied Electrochemistry (Beckman Bulletin 7738).

The mV mode may also be used with ion-selective electrodes. The relative mV mode can be used in the standard addition or standard subtraction method of ion analysis.

STANDARD SOLUTION(S)

Make up appropriate standard solution(s) to provide known voltage(s), depending on the reference electrode used and the temperature. For example, common standards used in redox measurements are pH 4 and pH 7 buffers saturated with quinhydrone.

mV MEASUREMENT PROCEDURE

1. Connect electrodes to appropriate inputs:
 - a. Connect indicating electrode to input marked "pH". A Pin-to-BNC Adaptor may be required as most metallic electrodes have a pin connector.
 - b. Connect reference electrode to input marked "REF".
2. Press **[ON]** to turn on instrument, then press **[C]** to clear. Display will show [CL AUTO].
3. Rinse electrodes with deionized water. Blot excess.
4. Immerse electrodes in desired solution. Press **[mV]**. Displayed value is absolute mV, as indicated by display of **[mV]**. When **[mV]** stops flashing, display will show [mV reading locked, **[mV]**].

RELATIVE mV MEASUREMENT PROCEDURE

1. Perform Steps 1 through 3 of mV MEASUREMENT PROCEDURE, above.
2. Immerse electrodes in standard solution to be used to establish the zero mV point. Press **[mV]**, then **[Z]**. When **[mV]** stops flashing, display will read [000.0 mV]. Note that, in mV mode, pressing **[Z]** causes the instrument to establish the zero mV point at the value of the current reading. If desired, this step may be repeated at any time to re-establish the zero mV point.
3. Rinse electrodes with deionized water. Blot excess.
4. Immerse electrodes in sample. Press **[mV]**. Displayed value is relative mV, as indicated by display of **[REL mV]**. When **[mV]** stops flashing, display will show [sample relative mV value locked, **[mV]**]. Absolute mV reading of the standard solution is automatically subtracted from the absolute mV reading of the sample, resulting in a relative mV reading for the sample.
5. If continuous readout of relative mV is desired, press **[HOLD]** to turn off Auto Read function.

NOTE

VOLTAGE DIFFERENCE BETWEEN STANDARD SOLUTION AND SAMPLE MUST NOT EXCEED 1000 mV. MAXIMUM DISPLAY RANGE IN mV MODE IS ± 999.9 mV.

NOTE

IN mV MODE, THE 59871S AUTOMATIC TEMPERATURE COMPENSATOR PROBE MAY BE USED FOR TEMPERATURE MEASUREMENT AND DISPLAY, BUT DOES NOT HAVE ANY TEMPERATURE-COMPENSATING EFFECT.

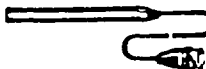
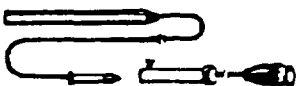
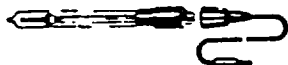

MEASURING CONCENTRATION (Φ12)


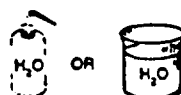


INSTRUMENT FUNCTIONS AND FEATURES

ELECTRODES, BUFFERS, AND ACCESSORIES

BATTERY REPLACEMENT, SERVICE AND TROUBLESHOOTING

**FOR ACCURATE CONCENTRATION MEASUREMENTS WITH THE $\Phi 12$,
THE FOLLOWING ITEMS ARE RECOMMENDED:**

1.  Ion-Selective electrode with BNC connector.
OR
- 1a.  Ion-Selective electrode with U.S. standard connector + U.S. standard-to-BNC adaptor.
2.  Reference electrode, Futura II.
Futura II cable with 2 mm pin connector.
NOTE: Depending on the application, a salt-bridge or double-junction electrode may be required.
3.  Two standard solutions of appropriate concentration, selected from the following values: 1.00, 2.50, 5.00, 10.00, 25.0, 50.0, 100.0, 250.0, 500, and 1000 units. Concentration can be expressed in any desired units such as ppm, mM, mg/L, and $\mu\text{g/L}$.
Make up these solutions per procedure or by diluting a stock solution to suit your requirement.
NOTE
CONCENTRATION UNITS FOR BOTH STANDARD SOLUTIONS MUST BE THE SAME AS DESIRED FOR SAMPLE READINGS.

4.  Two clean beakers or equivalent containers, approximately 100-250 mL, for containing the two standard solutions.
5.  Squirt bottle or beaker containing deionized or distilled water for rinsing electrodes.
6.  Clean towels, "Kwadraps", etc., for blotting electrodes.
7.  SAMPLE
The sample to be measured.

For part numbers, see "Electrodes, Buffers, and Accessories."
For concentration measurement procedure, see next page.

MEASURING CONCENTRATION ($\Phi 12$)

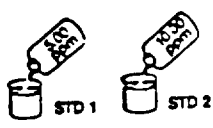

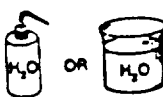
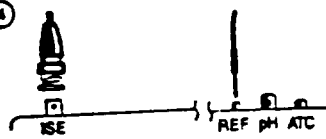
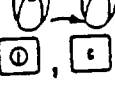
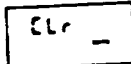
INSTRUMENT FUNCTIONS AND FEATURES

ELECTRODES, BUFFERS, AND ACCESSORIES



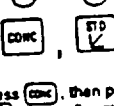
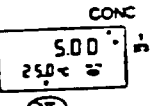


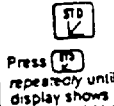
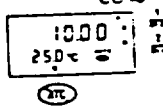
BATTERY REPLACEMENT, SERVICE AND TROUBLESHOOTING

CONCENTRATION MEASUREMENT FOR TWO-STANDARD OPERATION




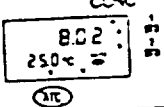
I. SETUP

<p>①</p>  <p>Prepare standard solutions. (e.g., 5.00 and 10.00 units).</p>	<p>②</p>  <p>Prepare sample.</p>	<p>③</p>  <p>Prepare deionized or distilled water for electrode rinse.</p>
<p>④</p>  <p>Connect electrodes to instrument.</p>	<p>⑤</p>  <p>Turn on and clear instrument.</p>	<p>⑥ Display will read:</p> 

II. STANDARDIZE

<p>①</p>  <p>Rinse electrodes. Blot excess H₂O.</p>	<p>②</p>  <p>Immerse electrodes in Standard 1. Stir briefly.</p>	<p>③</p>  <p>Press CONC, then press STD repeatedly until display shows Standard 1 value, e.g., 5.00.</p>	<p>④ When STD stops flashing, proceed.</p> 
<p>⑤</p>  <p>Rinse electrodes. Blot excess.</p>	<p>⑥</p>  <p>Immerse electrodes in Standard 2. Stir briefly.</p>	<p>⑦</p>  <p>Press STD repeatedly until display shows Standard 2 Value, e.g., 10.00.</p>	<p>⑧ When STD stops flashing, proceed.</p> 

III. MEASURE CONCENTRATION

<p>①</p>  <p>Rinse electrodes. Blot excess.</p>	<p>②</p>  <p>Immerse electrodes in sample. Stir briefly.</p>	<p>③</p>  <p>Press CONC.</p>	<p>④ After CONC stops flashing, display will read concentration of sample.</p> 
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FOR MORE DETAILED INSTRUCTIONS ON CONCENTRATION MEASUREMENT, PROCEED TO NEXT PAGE.

INSTRUMENT FUNCTIONS AND FEATURES
ELECTRODES, BUFFERS, AND ACCESSORIES

CONCENTRATION MEASUREMENT PROCEDURE

The following procedure, utilizing two-point standardization, can be used to measure concentrations of ions in almost any desired units.

STANDARD SOLUTIONS:

Standards can be made from any type of solution, with concentrations selected from the following values: 1.00, 2.50, 5.00, 10.00, 25.0, 50.0, 100.0, 250.0, 500, and 1000 units.

Units of concentration may be any that the user finds convenient. CONCENTRATION UNITS FOR BOTH STANDARD SOLUTIONS MUST BE THE SAME AS DESIRED FOR SAMPLE READINGS.

Some examples of units are: parts per million, percent, moles per liter, parts per billion, milliequivalents per liter, and ounces per gallon.

Select two standard values as close as possible to the anticipated sample value, preferably with one standard value below and one standard value above the sample. For example, if sample solution is about 150 millimoles per liter (mM), make up standards of 100 mM and 250 mM. If sample concentration varies widely, for example, between 10 molar and 75 molar, make up standards of 10 molar and 100 molar.

Standards and samples should be at the same temperature to avoid temperature-dependent variations in readings.

NOTE

Standard and sample solutions may require ionic strength adjustment or interfering ion removal. Consult electrode instructions for details.

CONCENTRATION MEASUREMENT PROCEDURE:

1. Connect electrodes to appropriate inputs:
 - a. Connect ion-selective electrode to input marked "ISE".
 - b. Connect reference electrode to input marked "REF".

NOTE

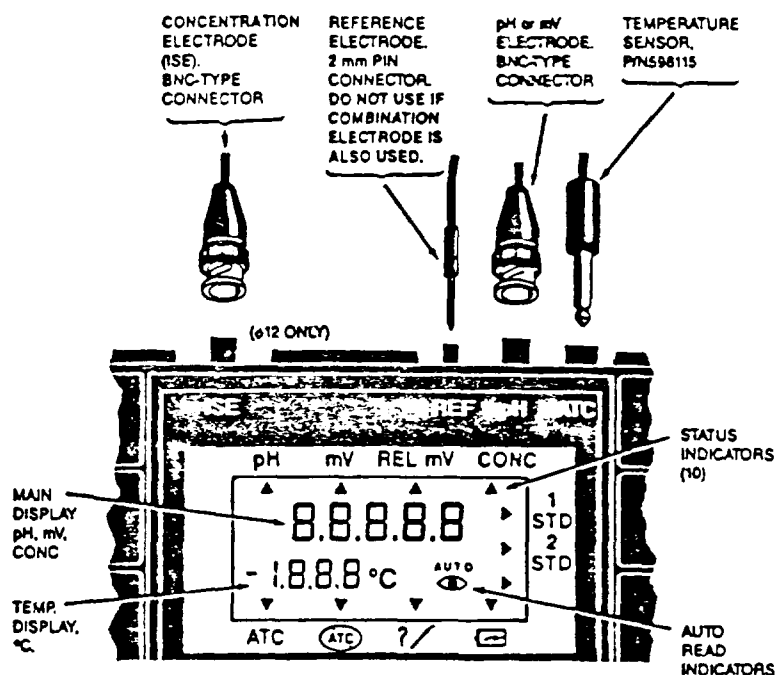
If, in addition to the ion-selective electrode, a combination pH electrode is connected to the instrument AND is to be immersed in the same solution, DO NOT use a separate reference electrode.

2. Press **[ON]** to turn on instrument, then press **[C]** to clear. Display will show [Ck, AUTO].
3. Rinse electrodes with deionized water. Blot excess.
4. Immerse electrodes in first standard solution. Press **[CONC]**, then press **[ST]** as many times as needed for the concentration value of the first standard to show on the display. When **[ST]** is pressed repeatedly, the display steps through the following values: 1.00, 2.50, 5.00, 10, 25, 50, 100, 250, 500, and 1000 concentration units. For example, if the concentration of the standard is 100 units, press **[ST]** seven times and the display will show [100]. When [**CD**] stops flashing, display will show [100 locked, **CD**].
5. Rinse electrodes with deionized water. Blot excess.
6. Immerse electrodes in second standard solution. The first and second standards must be different, but can be measured in any order. Press **[ST]** as many times as needed for the display to show the concentration value of the second standard, e.g., 250. When [**CD**] stops flashing, display will show [250 locked, **CD**].
7. Rinse electrodes with deionized water. Blot excess.
8. Immerse electrodes in sample. Press **[CONC]**. When [**CD**] stops flashing, display will show [sample value locked, **CD**]. Measurement is now complete. Repeat Steps 7 and 8, above, for additional samples.
9. If continuous concentration readout is desired, press **[AUTO]** to turn off Auto Read function.

INSTRUMENT FUNCTIONS AND FEATURES

ELECTRODES, BUFFERS, AND ACCESSORIES

ELECTRODE CONNECTIONS



DISPLAY FEATURES AND STATUS INDICATORS

DISPLAY

- The large digits show the following:
1. Readout of the measured variable: pH, mV, or concentration.
 2. [Clr] is displayed, indicating that instrument is cleared, when [C] is pressed.
 3. Error message:

[Er] indicates an excessive, potentially damaging, input voltage, typically caused by static electricity when the electrode pair is not in solution. In this case, immerse electrodes in solution, press [C], and proceed with measurement. If [Er] again appears, check connections and electrodes for possible open circuit.

Temperature Display The small digits display temperature in °C. Will read 25 °C if ATC not plugged in. (°C)

AUTO AUTO READ ON/OFF Indicator for AUTO READ ON/OFF Key described subsequently.

AUTO READ Status Indicator (eye symbol). Functions during standardization and when instrument is in AUTO mode. During standardization, the eye symbol starts flashing when [STO] is pressed, and locks on when the reading has stabilized. During sample measurement in AUTO mode, the eye symbol starts flashing when a mode key is pressed, and locks on when the reading has stabilized. The reading remains locked until a mode key is pressed. If an interval of approximately 30 minutes elapses without a key being pressed, the instrument turns off automatically to conserve the batteries, but retains all standardization data in memory.

STATUS INDICATORS

ATC Indicates that ATC is plugged in. The instrument measures and displays temperature within the range of -5 °C and 100 °C. Display of [Er] indicates that the temperature sensed is outside the measurement range, or the ATC is nonfunctional.

ATC Indicates that ATC is not plugged in. The temperature reading defaults to 25 °C.

pH Indicates that instrument is in pH mode.

mV Indicates that instrument is in mV mode.

REL mV Indicates that instrument is in relative mV mode.

φ11 and φ12 only

CONC Indicates that instrument is in concentration mode. φ12 only.

1 STD Indicates that one standard has been used to standardize for the selected measurement mode (pH or CONC).

2 STD Indicates that two standards have been used to standardize for the selected measurement mode (pH or CONC).

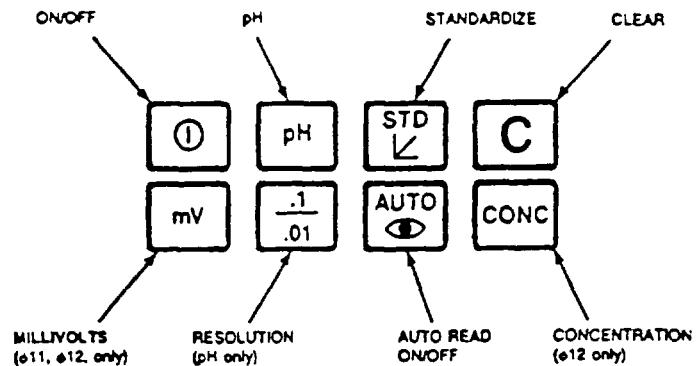
?/ Indicates a questionable electrode and/or standardization.

Indicates that batteries should be replaced.

INSTRUMENT FUNCTIONS AND FEATURES

ELECTRODES, BUFFERS, AND ACCESSORIES

KEYPAD



KEYPAD FUNCTIONS

KEY

- ①** Instrument ON/OFF Key. When OFF, the instrument retains the standardization data in memory. Instrument shuts off automatically after 30 minutes of inactivity if AUTO READ is ON. (See below.)
- C** Clear Key. Clears instrument, resetting all standardization data to default values, and returning instrument to AUTO Mode.
- AUTO** Auto Read Key. Turns Auto Read function ON and OFF:
 1. When Auto Read is ON:
 - a. The word [AUTO] appears on the display.
 - b. The instrument tests the electrode signal for stability. During this test, [CD] flashes ON and OFF. When the signal has met the stability requirement (see SPECIFICATIONS), [CD] remains on continuously, and the digital display locks onto the reading. No further measurements are made until a key is pressed.
 - c. After 30 minutes without keypad input, the instrument turns off automatically but retains all standardization data.
 2. When Auto Read is OFF:
 - a. [AUTO] disappears from display.
 - b. The instrument continuously measures and displays in the selected mode: pH, mV, or CONC.
 - c. After 1 to 2 hours without keypad input, the instrument turns off automatically but retains all standardization data.
- 0.1 / 0.01** pH Resolution Selection Key. Changes resolution of the displayed pH reading from 0.1 to 0.01 pH unit, or vice versa. At the lower resolution (0.1), time required for the Auto Read to lock is shorter. (See SPECIFICATIONS).
- pH** Selects the pH measurement mode.
- mV** Selects the mV mode (pH 11, pH 12), for measurement of either absolute or relative millivolts. See MEASURING mV AND RELATIVE mV.
- CONC** Selects the concentration measurement mode (pH 12). Used with specific ion electrodes.
- STD** Standardize Key. Standardizes instrument. Depends upon mode:
 - a. pH Mode: [STD] Key causes the instrument to automatically identify the pH value of the buffer from any one of the following: 1.68, 4.00, 7.00, 10.01, and 12.45.
 - b. mV Mode (pH 11, pH 12): [STD] Key causes the instrument to establish the zero-millivolt level at the value of the current reading. Instrument is now in Relative mV mode.
 - c. CONC Mode (pH 12): Repeated pressing of [STD] Key causes the instrument to step through the following sequence of values: 1.00, 2.50, 5.00, 10, 25, 50, 100, 250, 500, and 1000 concentration units.

1. FUTURA II ELECTRODES

COMBINATION ELECTRODES:

	Standard 8" x 1/2"	Probe 8-10" x 3/8"	Test-Tube 8-9" x 5-6mm
Glass Body Ag/AgCl, Refillable	39520	39521	39522
Glass Body Calomel, Refillable	39527	39528	39525, 39526 (7")
Epoxy Body Calomel, Refillable	39838	—	39839
Epoxy Body Ag/AgCl, Refillable	39831	39833	39835
Epoxy Body Ag/AgCl, Gel Filled	39836	39832	39834
Epoxy Body, Star Ag/AgCl Refillable	39837		
Glass Body, Star Ag/AgCl Refillable	39524		
Flat Bulb, Epoxy Body	39523		

ELECTRODE PAIRS:

pH INDICATING ELECTRODES:

0-14 pH, Spherical Bulb	39314
0-11 pH, Dome Bulb (Durable)	39316

METALLIC ELECTRODES:

Silver Billet	39281
Platinum Inlay	39273

REFERENCE ELECTRODES:

Calomel Half Cell, Quartz Fiber Junction	39418
Calomel Half Cell, Ceramic Fill Junction	39417
Ag/AgCl Half Cell, Quartz Fiber Junction	39418
Calomel Half Cell, Sleeve Double Junction	39419
Calomel Half Cell, Inverted Sleeve Junction	39420
Ag/AgCl Half Cell, Inverted Sleeve Junction	39421

2. FUTURA II KEEPER CABLES

COMBINATION AND INDICATING ELECTRODE CABLES

1m, BNC Connector	597578
2m, BNC Connector	597579
6m, BNC Connector	597580

REFERENCE ELECTRODE KEEPER CABLES

1m, 2mm Pin Connector	598982
2m, 2mm Pin Connector	598983
6m, 2mm Pin Connector	598984

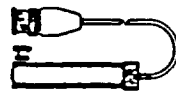
3. SALT BRIDGE: 563853

4. SUBMERSIBLE COMBINATION pH ELECTRODE WITH ATC: 39530

5. AUTOMATIC TEMPERATURE COMPENSATOR, 598115:

Permits temperature measurement and display, and temperature compensation of pH and ion-selective electrodes, within range of -5°C to 100°C. Epoxy body. For use with standard 5-inch (13-cm) electrodes. Includes 39" (1 meter) cable with miniature phone jack.

6. ELECTRODE ADAPTORS:



592362 Standard to
BNC Adaptor

Adapts Glass Electrode (GE) BNC terminal on
pH Series pH Meters to accommodate
electrodes with U.S. Standard Connectors.



592367 PIN to BNC Adaptor

Adapts Glass Electrode (GE) BNC terminal on
pH Series pH Meters to accommodate
electrodes with PIN Connectors.
Typically used to connect metallic electrodes.

7. BUFFERS

	6 Pack of Pints	1 Gallon	5 Gallons	Powder (Colorless)
pH 4 Buffer (red)	582517	566001	582822	3005
pH 7 Buffer (green)	582521	566003	582823	3007
pH 10 Buffer (blue)	582525	566005	582824	3019
pH 12.45				3010

8. FILLING SOLUTIONS

Description	Quantity	Part No.
Combination Electrode Filling Solution or Ag/AgCl Reference Electrode Filling Solution (4M KCl/AgCl saturated; to be used with Ag/AgCl internals)	4-pack of 100 mL bottles	566467
Reference Electrode Filling Solution (saturated KCl to be used with Calomel internals)	4-pack of 100 mL bottles	566468
Electrode Soaking Solution	4-pack of 100 mL bottles	566576
Salt Bridge Solution, Contains Sodium Nitrate and Sodium Acetate	4-pack of 100 mL bottles	566469
Filling Solution, 1M, KCl Saturated with AgCl (Star-Series electrodes only)	4-pack of 100 mL bottles	598943

9. pH START-UP KIT:

39831 Electrode, Cable, Thermocompensator, Sample Buffers, Filling solution	Part No. 123135
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10. pH STAND LAB ORGANIZER

123136

11. pH DELUXE FIELD CASE

123128

12. pH SOFT CASE

123127

13. pH MOUNT, WALL/SHELF BRACKET

599190

Your 410, 11, or 12 is powered by two 3.6 volt lithium batteries. Expected battery life is over 1,000 hours of continuous operation. Replacement batteries can be obtained by ordering Part No. 845754 from your local Beckman office. (In U.S. call 1-800-742-2345).

Acceptable replacement batteries are also available on a world-wide basis:


Mfr.
Electrochem Industries
Power Conversion Inc.
Salt Advanced Battery Div.
Tadiran

Part No.
32940-TC
T08-41
LS6
TL-2100 AA/S

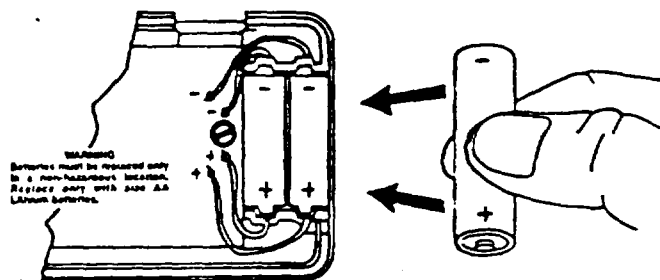
945574

Local suppliers may be found in your telephone directory.


Note that these batteries are 3.6 volt lithium cells. Do not attempt to replace them with 1.5 volt alkaline or carbon-zinc cells.

If instrument display indicates low battery voltage  or if display is blank when instrument is turned on, batteries should be replaced:



1. Remove 2 Phillips screws and bottom cover from instrument.
2. Lift out old batteries.
3. Note (+) and (-) markings in battery compartment.
4. Check (+) and (-) markings on batteries and insert as shown:

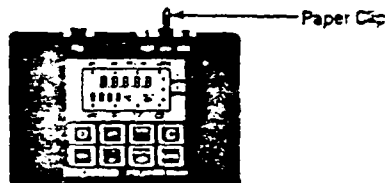




5. Replace back cover and screws.

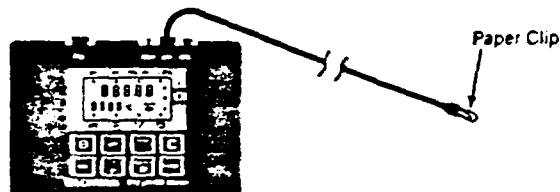
IMPORTANT: A "BREAK-IN" PERIOD OF UP TO 30 MINUTES IS REQUIRED WHEN SOME NEW LITHIUM BATTERIES ARE FIRST PLACED INTO SERVICE. DURING THIS PERIOD, THE LOW BATTERY SYMBOL AND SOME "GHOSTING" MAY APPEAR ON THE DISPLAY. IF SO, LEAVE INSTRUMENT ON FOR 20-30 MINUTES AND THEN PRESS . THE LOW BATTERY SYMBOL AND "GHOSTING" SHOULD DISAPPEAR.




TROUBLESHOOTING PROCEDURE

1. Disconnect electrode cable(s) from instrument. Press  to turn on instrument, then press  to clear. Display should show [Clr, AUTO]. If not, replace batteries per BATTERY REPLACEMENT, above. If instrument is still inoperative, call Service Hot Line: 1-800-662-6217.
2. Insert one end of a paper clip into the small hole in the center of the "pH" input connector. Hold the other end of the clip to the inside barrel of the same connector as shown.



3. Press  then . The display should lock at pH 7.00, indicating a one-point standardization.
 - a. If instrument passes test, go to Step 4.
 - b. If instrument fails test, call Service Hot Line: 1-800-662-6217.
4. Reconnect pH electrode cable to "pH" input connector. Short the input connector of the cable.



Press  and then . Display should lock at pH 7.00. Press , then remove paper clip. Reading should drift.

- a. If instrument passes test, go to Step 5.
- b. If instrument fails test, call Beckman Electrochemistry Applications:
1-800-654-8067 Outside California
714-871-4848 Within California

5. Reconnect pH electrode(s). Immerse electrode(s) in pH 4 buffer and perform one-point standardization. Then immerse electrode(s) in pH 10 buffer and take pH reading. At 25°C, the reading should be between 9.7 and 10.1 pH.
 - a. If the test is passed, the pH meter, cable, and electrode(s) are functioning properly.

INSTRUMENT BECKMAN PART NO.	pH 10 123132	pH 11 123133	pH 12 123134
pH MEASUREMENT			
Range	0 to 15.99 pH	0 to 15.99 pH	0 to 15.99 pH
Resolution (Selectable)	0.01, 0.1 pH unit	0.01, 0.1 pH unit	0.01, 0.1 pH unit
Relative Accuracy	± 0.01 pH	± 0.01 pH	± 0.01 pH
Auto Read Mode	0.1 pH Resolution: Display locks after reading is stable within 1.0 mV for 4 seconds. 0.01 pH Resolution: Display locks after reading is stable within 0.5 mV for 8 seconds.		
Buffers Recognized by Instrument: 1.68, 4.00, 7.00, 10.01, 12.45 pH.			
MILLIVOLT MEASUREMENT			
Range	—	-999.9 to +999.9 mV	-999.9 to +999.9 mV
Resolution	—	0.1 mV	0.1 mV
Accuracy	—	± 0.2 mV ± 0.02% of reading, relative mV	± 0.2 mV ± 0.02% of reading, relative mV
Auto Read Mode	—	Display locks after reading is stable within 0.5 mV for 8 seconds.	
CONCENTRATION MEASUREMENT			
mV Accuracy	—	—	± 0.1 mV
Auto Read Mode	—	—	Display locks after reading is stable within 0.25 mV for 8 seconds.
Useable Standard Values	—	—	Two values, in any desired units, selected from the following: 1.0, 2.5, 5.0, 10, 25, 50, 100, 250, 500, and 1000.

TEMPERATURE MEASUREMENT (ALL MODELS)
Range: -5°C to 100°C
Resolution: 0.1°C
Accuracy (with Beckman 598115 Probe): ± 0.5°C
MISCELLANEOUS (ALL MODELS)
Input Connections:
1. BNC input for pH, mV, and concentration.
2. 2-mm pin connector for reference electrode.
3. Miniature phone jack for Beckman 598115 Automatic Temperature Compensator.
Operating Temperature: 15°C to 40°C, ambient, non-condensing.
Power Source: Two lithium cells, 3.6 volts each, AA Size.
Error Indications:
1. Input overvoltage (all modes)
2. Temperature compensation non-functional
3. Low batteries
4. Questionable electrode/standardization.
Size: 5.2 inches x 3.8 inches x 1.3 inches.

Beckman Co
National
West Poplar Ave
OK 93257

Instructions

E-11

Platinum Combination Electrode

Catalog No. 13-639-82

The Fisher platinum combination electrode combines a silver/silver chloride reference element and a platinum-wire indicating element in a single probe. This "dual element" configuration eliminates the need for two separate electrodes and is especially applicable to measurements in narrow-neck flasks and other restricted-entry receptacles.

The platinum combination electrode is recommended for use with automatic titrators and similar electroanalytical equipment. The close physical proximity of the porous-plug liquid junction to the platinum-wire indicator section results in reduced resistance between these elements and produces a rapid dynamic response for both redox measurements and potentiometric titrations. Additionally, the electrode is ideally suited for any application that involves the measurement of oxidation-reduction potentials or requires the use of a "noble metal" sensor.

The electrode measures 5 inches with a 30-inch lead, and functions over a -5° to 110°C temperature range. The filling solution is 4M KCl saturated with AgCl (Fisher No. So-P-135), and flow rate at the junction is less than $8\ \mu\text{l}$ per hour at an 8 cm head. Reference output is $44 \pm 1\text{mV}$ vs. S.C.E., while junction resistance is less than 10K ohms.

INSTALLATION

Place the platinum combination electrode into service as follows:

1. Remove cap from supplied filling-solution bottle, and screw on dispenser spout.
2. Lower rubber sleeve on electrode body until filling hole is exposed, and fill reference cavity with electrolyte until meniscus reaches a level approximately $\frac{1}{4}$ -inch below filling hole.

NOTE: Always use 4M KCl solution saturated with AgCl (Fisher No. So-P-135) as the electrolyte. NEVER USE SATURATED KCl FILLING SOLUTION.

3. Place electrode upright in empty beaker to permit filling solution to wet and flow through porous plug, as evidenced by formation of KCl crystals on outer surface of plug.

NOTE: If no flow is observed within 30 minutes, or if response is unsatisfactory during an analysis, soak electrode in dilute KCl (0.1M) for several hours, and then perform the following procedure:

- a. Hold electrode (cap up) at a 45° angle between thumb and forefinger on left hand, so that filling hole faces out and is directly opposite base of thumb.
- b. Insert dispensing spout into filling hole.
- c. Make sure that electrode is supported by base of thumb, then firmly press spout into filling hole to make an airtight seal.

NOTE: Normally, spout tip will not touch internal element; while applying pressure, however, care should be exercised to prevent contact. If necessary, cut off a portion of the tip.

- d. While maintaining seal, squeeze filling bottle firmly so

that electrode becomes pressurized.

NOTE: A bead of liquid should form at liquid junction in about 30 seconds; in some cases, however, it may be necessary to maintain pressure for several minutes. If flow cannot be established, refer to REJUVENATION section.

4. Mount electrode on suitable holder and connect jacks to pH meter.

OPERATION

For optimum operation with the platinum combination electrode, observe the following general procedures:

1. Rubber sleeve should always be lowered on electrode body to expose filling hole and permit proper electrolyte leakage.
2. Level of electrolyte must always be maintained above surface of sample solution to avoid backflow of sample into electrolyte. Refill reference cavity as required.
3. After removing electrode from one solution and before immersing in another, the outer surface should be rinsed with distilled water.

STORAGE

When not in use, store the platinum combination electrode as follows:

1. Slide rubber sleeve into position over the filling hole.
2. Place supplied cot over tip of electrode by threading platinum wire through opening and sliding cot onto glass body until porous plug is completely covered.

REJUVENATION

Rejuvenation of the platinum combination electrode may only require a simple cleaning. Occasionally, a more thorough cleaning is required, or the porous-plug junction may have to be unblocked. Each is covered separately below.

Simple Cleaning

A simple cleaning of the electrode is done as follows:

1. Wash electrode surface with a good detergent.
NOTE: RBS-25 detergent (Fisher No. So-C-181) is recommended.
2. Polish platinum wire with scouring powder.
3. Rinse electrode thoroughly with distilled water.

Thorough Cleaning

For a more thorough cleaning, perform the following:

1. Connect tip of large cable plug to negative terminal of a 22V dry cell, then immerse tip of electrode in a 1N solution of hydrochloric acid.
2. Similarly connect a platinum or graphite electrode to positive terminal of dry cell and immerse tip of electrode in same solution.

NOTE: Hydrogen will evolve rapidly, and the metallic electrode will be cleaned by electrolysis in 5 to 10 seconds.

3. After cleaning, disconnect both electrodes and rinse



each with distilled water.

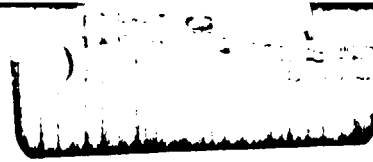
Unblocking the Junction

If the liquid junction should become partially blocked, perform the following:

1. Inspect reference cavity for crystallization.
2. If crystals are evident, proceed as follows:
 - a. Remove filling solution by shaking it out through filling hole.
 - b. Rinse cavity repeatedly with distilled water until all crystals are dissolved.
 - c. Refill cavity with fresh 4M KCl solution saturated with AgCl (Fisher No. So-P-135).

CAUTION: Never use saturated KCl as the electrolyte.

- d. Repeat all of step 3 under INSTALLATION.
3. If difficulty persists, perform the following in sequence depending upon the severity of the blockage:
 - a. Soak electrode overnight in dilute KCl (0.1M).
 - b. Boil junction in dilute KCl for 5 to 10 minutes.
 - c. Carefully sand or file the porous plug junction.



APPENDIX C
MODIFICATION TO APPENDIX F OF ORIGINAL QAPP

Appendix F - Warzyn Engineering Inc. Laboratories Standard Operating
Procedures Using Non-CLP Protocols

This appendix should be ammended to include protocols and criteria contained in Appendix C of this QAPP Addendum.

APPENDIX C QAPP ADDENDUM

ANALYTICAL METHODS USED BY WARZYN FOR THE AMERICAN CHEMICAL SERVICES RI/FS

The following are standard operating procedures for analyses to be performed by Warzyn on samples from The American Chemical Services Site. Methods list detection limits and numbers of quality control (QC) samples to be performed, but do not specify performance standards. The following table lists frequency and performance standards for QC samples. Quality control criteria will follow EPA SOW 7/88 as written. When an analyte concentration exceeds the calibrated range, re-analysis of the prepared sample after appropriate dilution is required. Methods for metals include flame and furnace SOPs for certain parameters. The appropriate method will be used to achieve desired detection limits. Arsenic and selenium will be performed by furnace techniques.

A standard at twice the detection limit (DL) will be analyzed for sulfate, chloride and alkalinity. The standards will not be used for instrument calibration, but will be used as a quality control sample to verify the DL. The DL standard will be analyzed at the beginning of each run.

Attachment 1

PARAMETER	AUDIT	FREQUENCY*	LIMITS
Metals-all matrices (except Hg)	Lab blank	1 per sample set	< detection limit
Metals, Mercury, Cyanide			
SOW Criteria 7/88			
Chloride	Lab blank	1 per 10	< 1 mg/l
	Check standard	1 per 10 samples and end of run	90-110% recovery
	Duplicate	1 per 10 samples	<20% RPD or < 1 mg/L
	Matrix spike	1 per 10 samples	85-115% recovery
	EPA QC Reference Standard	1 per set	95% confidence interval
Total Alkalinity	Lab Blank	1 per 10	<5 mg/L
	Check standard	1 per 10 samples and end of run	90-110% recovery
	Duplicate	1 per 10 samples	<20% RPD or <5 mg/L
	Matrix spike	1 per 10 samples	85-115% recovery
	EPA QC Reference STD	1 per set	95% confidence interval
COD			
	Lab blank	1 per 10	<20 mg/L
	Duplicate	1 per 10 samples	<20% RPD or <20 mg/L
	Calibration check STD	1 per 10 samples and end of run	90-110% recovery
	Matrix spike	1 per 10 samples	85-115% recovery

	EPA QC Reference STD	1 per set	95% confidence interval
NH ₃ -N	Lab blank	1 per 10	<0.10 mg/L
	Duplicate	1 per 10 samples	<20% RPD or <0.10 mg/L
	Calibration check STD	1 per 10 samples and end of run	90-110% recovery
	Matrix spike	1 per 10 samples	85-115% recovery
	EPA QC Reference STD	1 per set	95% confidence interval
NO ₃ + NO ₂ -N	Lab blank	1 per 10	<0.02 mg/l
	Check standard	1 per 10 samples and end of run	90-110% recovery
	Duplicate	1 per 10 samples	<20% RPD or <0.02 mg/L
	Matrix spike	1 per 10 samples	85-115% recovery
	EPA QC Reference Standard	1 per set	95% confidence interval
SO ₄	Lab Blank	1 per 10	<5 mg/L
	Check standard	1 per 10 samples and end of run	90-110% recovery
	Duplicate	1 per 10 samples	<20% RPD or <5 mg/L
	Matrix spike	1 per 10 samples	85-115% recovery
	EPA QC Reference STD	1 per set	95% confidence interval
Total Cyanide	Lab blank	1 per 10	< 0.01 mg/L
	Duplicate	1 per 10	20% RPD or <0.01 mg/L
	Calibration check STD	1 per 10 and end of set	85-115% recovery
	Matrix spike	1 per 10	85-115% recovery
	EPA QC Reference STD	1 per set	95% confidence interval

TOC	Lab blank	1 per 10	< 1.0 mg/L
	Duplicate	1 per 10	20% RPD or <1.0 mg/L
	Calibration check STD	1 per 10 and end of set	85-115% recovery
	Matrix spike	1 per 10	85-115% recovery
	EPA QC Reference STD	1 per set	95% confidence interval
TDS	Lab blank	1 per 10	<20 mg/L
	Duplicate	1 per 10 samples	20% RPD or <20 mg/L
	EPA QC Reference STD	1 per set	95% confidence interval
TSS	Lab blank	1 per 10	<2 mg/L
	Duplicate	1 per 10	20% RPD or <2 mg/L
	EPA QC Reference STD	1 per set	95% confidence interval
Grain size	Lab Duplicate	1 per 10	20% RPD or <2% by weight
Atterburg Limits	Lab Duplicate	1 per 10	20% RPD or <2% by weight
Permeability	Field Duplicate	1 per 10	50% RPD
Cation Exchange Capacity	Lab Duplicate	1 per 10	15% RPD

*Frequencies apply to each matrix individually.

ALKALINITY - AUTOANALYZER

Scope and Application: This method is applicable to drinking water, surface water, groundwater and wastewater.

Reference: EPA 1983, Method 310.2
Lachat Instruments 1986, Method 10-303-31-1-C

Sample Handling: Refrigerate at 4°C and analyze within 14 days of collection.

Detection Limit: 5.0 mg/L as CaCO_3

Optimum Concentration Range: 5.0 - 500 mg/L

Instrument Conditions:

1. Pump speed: 35
2. Cycle period: 60 seconds
3. Load period: 30 seconds
4. Inject period: 15 seconds
5. Inject to start of peak period: 10 seconds
6. Inject to end of peak period: 56 seconds
7. Gain: 150×10
8. Zero: 180
9. Interference filter: 410 nm
10. Sample loop: 90 cm
11. Standards for curve set-up: 0, 20.0, 50.0, 100, 250, 500 mg/L.

Reagent Preparation: (Prepare fresh every 6 months, unless otherwise stated.)

1. Degassed Milli-Q water - 2 options:
 - a. Boil Milli-Q water vigorously for 5 minutes. Cool and store in cubitainer.
 - b. Bubble helium, using the fritted gas dispersion tube, through the Milli-Q water (15 min/20 L.) Store in cubitainer.
2. Stock alkalinity standard (1000 mg/L as Na_2CO_3): In a 1 liter volumetric flask, dissolve 1.060 g of anhydrous primary standard grade sodium carbonate (Na_2CO_3 -dried at 140°C for 4 hours) in approximately 900 mL of helium purged Milli-Q water, and dilute to mark.

3. Standards: (Prepare fresh every 2 months). Dilute to volume using degassed MQ water. Refrigerate.

<u>Concentration of Standard</u>	<u>Letter Identifier</u>	<u>Volume of Alk. Stock</u>	<u>Dilute to</u>
0 mg/L	A	0	200 mL
20.0 mg/L	B	4.0	200 mL
50.0 mg/L	C	10.0	200 mL
100 mg/L	D	50.0	500 mL
250 mg/L	E	125.0	500 mL
500 mg/L	F	100.0	200 mL

NOTE: Final volumes are not the same!
Computer refers to standards by letter.

4. Sodium hydroxide (0.1M): In a 1 liter flask, dissolve 4.0 g sodium hydroxide (NaOH) and dilute to the mark with Milli-Q water.
5. Hydrochloric acid (0.1M): In a 1 liter flask, dilute 8.3 mL of concentrated HCL in Milli-Q water and dilute to the mark.
6. KHP buffer (25.0 mM, pH 3.1): In a 1 liter flask, dissolve 5.10 g of potassium acid phthalate (KHP) ($\text{KHC}_2\text{H}_3\text{O}_4$) in approximately 500 mL of helium purged Milli-Q water. Add 87.6 mL of 0.1M HCL and dilute to the mark. Adjust the pH of the buffer to 3.1 with 0.1M HCL or 0.1M NaOH. Vacuum filter through a 0.45 micron membrane filter before each use. STORE IN GLASS AND PREPARE MONTHLY!
7. Methyl orange reagent: In a 1 liter volumetric flask, dissolve 0.125 g of methyl orange indicator in about 700 mL of Milli-Q water and dilute to the mark. Mix well and vacuum filter through a 0.45 micron membrane filter before each use. Store in amber glass! NOTE: Amount of methyl orange may be adjusted for variances in lots of methyl orange.

Notes:

1. Samples must be diluted to obtain concentrations within the optimum working range.
2. The gain and zero settings are guidelines and must be adjusted each day to optimize.
3. The alkalinity standards can be combined with chloride and sulfate standards for use with the 3 channel method.
4. Turbidity will interfere. Samples must be filtered prior to analysis. (Use Whatman #1 or #4.)
5. Color will interfere, dilute the sample and also spike the dilution to confirm the quality of the result.

System Operation:

- A. Refer to "Auto Analyzer Operation start-up procedure." (IOP# LAA-Section A).
- B. Analyze an initial calibration standard, a blank, and a known reference standard at the beginning of each run. The blank must be below the detection limit and the standards must be within required control limits before any samples are analyzed.
- C. Spike samples by mixing sample with an equal volume of 250 mg/L standard (E), for a final spike level of 125 mg/L.
- D. The calibration check standard is 100 mg/L (D).
- E. Refer to "Auto Analyzer shut-down procedure". (IOP# LAA-Section B).

Quality Control:

1. Establish a standard curve with the standards listed above. The derived concentration of each calibration must be $\pm 10\%$ of the true value.
2. A quality control calibration standard of 100 mg/L and a calibration blank are to be analyzed, at a minimum, after every 10 samples. If less than 10 samples are analyzed, a calibration standard and blank are still required. The last samples analyzed in the run are to be the calibration standard and blank. These standards must be within the acceptable ranges or the samples run after the last acceptable check standard are to be reanalyzed.
3. Duplicate and spike a minimum of 1 out of 10 samples. If less than 10 samples are analyzed, a duplicate and spike are still required. Spike recoveries and duplicates are to be within acceptable ranges or data must be flagged appropriately.

Calculation:

1. Calculate with Lachat QuikChem software, in the concentration mode, using the IBM XT computer. See LAAC SOP for further detail.

CHLORIDE - AUTOANALYZER

Scope and Application: This method is applicable to drinking water, surface water, groundwater and wastewater.

Reference: EPA 1983, Method 325.2
Lachat Instruments 1986, Method 10-117-07-1-B

Sample Handling: Refrigerate at 4°C and analyze within 28 days of collection.

Detection Limit: 1.0 mg/L.

Optimum Concentration Range: 1.0 - 100 mg/L

Instrument Conditions:

1. Pump speed: 35
2. Cycle speed: 30 seconds
3. Load period: 15 seconds
4. Inject period: 15 seconds
5. Inject to start of peak period: 8 seconds
6. Inject to end of peak period: 31 seconds
7. Gain: 200
8. Zero: 250
9. Interference filter: 480 nm
10. Sample loop: 20 cm
11. Standards for curve set-up: 0, 10.0, 20.0, 50.0, 80.0, and 100 mg/L Cl.

Reagent Preparation: (Prepare fresh every 6 months, unless otherwise stated.)

1. Degassed Milli-Q water - 2 options:

- a. Boil Milli-Q water vigorously for 5 minutes. Cool and store in cubitainer.
- b. Bubble helium, using the fritted gas dispersion tube, through the Milli-Q water (15 min/20 L.) Store in cubitainer.

2. Stock chloride standard (1000 mg/L): In a 1 liter volumetric flask, dissolve 1.648 g of primary grade sodium chloride (NaCl), previously dried at 103°C, in 500 mL D.I. water. Dilute to the mark and invert to mix. Refrigerate.

3. Standards: (Prepare fresh every 2 months). Dilute volume using D.I. water. Refrigerate.

<u>Concentration of Standard</u>	<u>Letter Identifier</u>	<u>Volume of Chloride Stock (ml)</u>	<u>Dilute to</u>
0 mg/L	A	0	200 mL
10.0 mg/L	B	2.0	200 mL
20.0 mg/L	C	4.0	200 mL
50.0 mg/L	D	25.0	500 mL
80.0 mg/L	E	40.0	500 mL
100 mg/L	F	20.0	200 mL

NOTE: Computer refers to standards by letter.
Final volumes are not the same!

4. Sodium mercuric thiocyanate reagent: In a 1 liter volumetric flask, dissolve 4.17 g of mercuric thiocyanate ($\text{Hg}(\text{SCN})_2$) in one liter of methanol. Invert to mix. Store in amber glass. Refrigerate.

CAUTION: Mercury is a very toxic metal. WEAR GLOVES!

5. Stock ferric nitrate reagent (0.5M): In a 1 liter volumetric flask, dissolve 202.0 g of ferric nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) in approximately 800 mL of deionized water. Add 25 mL of concentrated nitric acid and dilute to one liter. Invert to mix. Refrigerate.
6. Combined color reagent: Mix 150 mL of stock mercuric thiocyanate solution with 150 mL of stock ferric nitrate reagent and dilute to 1000 mL with deionized water. Vacuum filter through a 0.45 micron membrane filter. Store at room temperature. Do Not Refrigerate.

Notes:

1. Samples must be diluted to obtain concentrations within the optimum working range.
2. The gain and zero settings are guidelines and must be adjusted each day to optimize.
3. The chloride standards may be combined with alkalinity and sulfate standards for use with the 3 channel method.
4. Any sample with turbidity must be filtered prior to analysis. (Use Whatman #1 or #4.) Record on data sheet.
5. Color is an interference, dilute the sample and also spike this sample to confirm the quality of the result.

System Operation:

- A. Refer to "Auto Analyzer Operation start-up procedure." (IOP# LAA-Section A).
- B. Analyze an initial calibration check standard, a blank, and a reference standard at the beginning of each run. The blank must be below the IDL and the standards within control limits.
- C. To spike samples, mix equal volumes of sample and 80 mg/L Cl standard for a final spike level of 40 mg/L Cl.
- D. The calibration check standard is 50 mg/L (D).
- E. Refer to "Auto Analyzer shut-down procedure". (IOP# LAA-Section B).

Quality Control:

1. Establish a standard curve with the standards listed above. Note that the calibration curve is calculated in a "piece-wise" fashion and is not linear. Be sure that calibration points describe a smooth curve.
2. A quality control calibration standard of 50.0 mg/L and a blank are to be analyzed, at a minimum, after every 10 samples. If less than 10 samples are analyzed, a calibration standard and blank are still required. The last samples analyzed in the run are to be the calibration standard and blank. These standards must be within the acceptable ranges or the samples run after the last acceptable check standard are to be reanalyzed.
3. Duplicate and spike a minimum of 1 out of 10 samples. If less than 10 samples are analyzed, a duplicate and spike are still required. Spike recoveries and duplicates are to be within acceptable ranges or data must be flagged appropriately.

Calculation:

1. Calculate with Lachat QuikChem software, in the concentration mode, using the IBM XT computer. See LAA SOP for further detail.

CHEMICAL OXYGEN DEMAND

Scope and Application: This method is applicable to surface water, sewage, wastewater, and groundwater.

Method: Dichromate reflux, Colorimetric

Reference: EPA 1983, Method 410.4

Detection Limit: 20 mg/L

Optimum Range: 20-700 mg/L

Sample Handling: Preserve with sulfuric acid to a pH <2 and refrigerate at 4°C. Analyze within 28 days.

Reagents and Apparatus:

1. Dichromate - mercuric sulfate-sulfuric acid digestion solution
2. Silver sulfate-sulfuric acid catalyst solution
3. COD standard solutions
4. Block digester, set at 150°C
5. 16 x 100 mm culture tubes with teflon lined screw caps
6. Eppendorf macropipetter, 0-5 mL
7. Spectrophotometer, set at 600 nm wavelength with sipper cell
8. Eppendorf microliter pipetter, 10-100 µL
9. 2 Repipette Dispensers, 1000 mL
10. De-ionized water

Reagent Preparation: (Prepare fresh every 6 months, unless otherwise noted.)

1. Digestion Solution: Add 10.2 g of dried potassium dichromate ($K_2Cr_2O_7$), 33.3 g of mercuric sulfate ($HgSO_4$) and 167 mL of concentrated H_2SO_4 to about 500 mL of DI water; dilute to 1000 mL in a volumetric flask and stir until dissolved. Store in a dark place.
2. Silver Sulfate-Sulfuric Acid Catalyst Solution: Add 22.0 g of silver sulfate (Ag_2SO_4) to a 2.5L bottle of conc. H_2SO_4 . Stir to dissolve.
3. COD Stock Standard, 1000 mg/L: Carefully weigh 0.8500g of dried potassium acid phthalate (KHP), dissolve in DI water and dilute to 1 liter in a volumetric flask. Preserve the stock solution with H_2SO_4 (2 mL conc. H_2SO_4 / L of solution). Refrigerate.
4. Working COD Standards: (Prepare fresh monthly and refrigerate. All working standards should be preserved with H_2SO_4 , 0.2 mL conc. H_2SO_4 in 100 mL).
 - A. 700 mg/L Standard: To a 100 mL volumetric flask, add 70 mL of 1000 mg/L Stock Standard and dilute to the mark with DI water.
 - B. 300 mg/L COD Standard: To a 100 mL volumetric flask, add 30 mL of 1000 mg/L Stock Standard and dilute to the mark with DI water.

C. 100 mg/L COD Standard: To a 100 mL volumetric flask, add 10 mL of 1000 mg/L COD Stock Standard and dilute to the mark with DI water.

D. 50 mg/L COD Standard: To a 100 mL volumetric flask, add 5 mL of 1000 mg/L COD Stock Standard and dilute to the mark with DI water.

E. 20 mg/L COD Standard: To a 100 mL volumetric flask, add 2 mL of 1000 mg/L COD Intermediate Standard and dilute to the mark with DI water.

Notes:

1. If a dark green or turquoise color occurs when sample is added or when the tube is being heated; the sample is over the upper limit of the curve and must be diluted and redigested.
2. Interference: Chlorides represent a positive interference. Mercuric sulfate is added to the digestion tubes to complex the chloride. Mercuric sulfate can complex up to 2,000 mg/L chloride before reacting with dichromate in the sample. If chloride exceeds 2,000 mg/L, dilute the sample.
3. Reagents are corrosive and toxic. Avoid skin contact.
4. Store standards in the refrigerator.
5. Store the dichromate solution and prepared tubes in the dark.

Procedure:

1. All glassware is to be soap and water washed, tap rinsed and DI water rinsed prior to analysis. Rinse digestion tubes and caps with DI water prior to use. Caps deteriorate over time. Discard caps after 3 uses.
2. Into each tube, pipet exactly 1.5 mL of COD digestion solution, using repipettor dispenser.
3. Using the repipettor dispenser, pipet down the side into each tube exactly 3.5 mL of the silver sulfate-sulfuric acid solution. Avoid any mixing with the digestion solution. These tubes may be stored, with caps having teflon liners, indefinitely. Store in the dark!
4. Prepare a standard curve consisting of the following standards: 0, 20, 50, 100, 300, and 700 mg/L COD.

The standards are carried through the digestion step.

5. Analyze an initial calibration standard, a blank, and a reference standard at the beginning of each run.

6. Using the Oxford 0-5 mL pipet, add 2.5 mL of sample, standard, or blank to the tube. Be careful to avoid air bubbles in the pipet tip and to eject all of the sample. Cap tubes tightly and mix by inverting 10-12 times.

To Spike: In a disposable cup, place 2.5 mL sample, add 2.5 mL of the 300 mg/L standard. Mix well. Use 2.5 mL of this mixture for the spiked sample analysis.

7. Place tubes in a block heater at 150°C for 2 hours. Block heater should be preheated at least 1 hour prior to use.
8. Remove tubes from block heater. Cool to room temperature. Read the absorbance on spectrophotometer, set at 600 nm, using the sipper cell. Samples can be stored in refrigerator overnight and read the next day. Do not shake tubes. Be very careful not to aspirate any of the precipitate in the bottom of the tube. Initially zero with the blank standard.

Quality Control:

1. Establish a standard curve with the standards listed above plus a blank. Record the absorbance check standard in the absorbance check book. The absorbances should remain consistent from run to run. If not, necessary troubleshooting must be performed before continuing (check wavelength, spectrophotometer bulb, solution, etc.)
2. A quality control calibration standard of 100 mg/L COD and a blank are to be analyzed, initially and after every 10 samples. If less than 10 samples are analyzed, a calibration standard and blank are still required. The last samples analyzed in the run are to be the calibration standard and blank. These standards must be within the acceptable ranges or the samples run after the last acceptable check standard are to be reanalyzed.
3. Duplicate and spike a minimum of 1 out of 10 samples. If less than 10 samples are analyzed, a duplicate and spike are still required. Spike recoveries and duplicate results are to be within acceptable ranges, or data must be flagged appropriately.

Calculation:

1. Calculate using linear regression.

To Calculate Spike:

$$\% \text{ Recovery} = \frac{(2)(\text{spike value}) - (\text{sample value})}{300} \times 100$$

CYANIDE, TOTAL - DISTILLATION

Scope and Application: This method is applicable to the determination of cyanide in drinking water, surface water, ground-water, sludges, soils and industrial wastes.

Methods: Distillation, Automated Colorimetric

Reference: EPA 1983, Method 335.2

SW-846, Method 9010

Standard Methods, 16th Edition, Method 412

Detection Limit: 0.005 mg/L

Optimum Range: 0.005 - 0.40 mg/L

Sample Handling: Preserve with sodium hydroxide to pH >12 and refrigerate at 4°C. Analyze samples within 14 days.

Reagents and Apparatus:

1. Cyanide reflux distillation apparatus
2. 25 mL and 50 mL graduated cylinders
3. Vacuum pump
4. Heating mantle
5. 250 mL volumetric flasks
6. Sodium hydroxide
7. Sulfuric acid, concentrated
8. Magnesium chloride
9. Deionized water
10. Bismuth nitrate
11. Sulfamic acid
12. Acetic acid, concentrated
13. Sodium thiosulfate, crystals

Reagent Preparation: (Prepare fresh every 6 months, unless otherwise noted.)

1. Sodium Hydroxide (1.25N):

Dissolve 50.0 g NaOH in D.I. water and dilute to 1 liter in a volumetric flask. Store in a plastic bottle.

2. Magnesium Chloride Solution:

Dissolve 510.0 g $MgCl_2 \cdot 6H_2O$ in D.I. water and dilute to 1 liter. Store in a plastic bottle.

3. Stock Cyanide Solution (1000 mg/L):

Dissolve 0.6275 g KCN and 0.5 g KOH and dilute to 250 mL with D.I. water in a volumetric flask. Prepare fresh every month. CAUTION: TOXIC! Refrigerate.

4. Standard Cyanide Solution (5 mg/L):

Pipet 5 mL of stock cyanide solution into 1 L volumetric flask containing approximately 500 mL D.I. water and 2 mL of 10N NaOH as a preservative. Dilute to volume with DI water. Prepare fresh weekly. Refrigerate.

5. Bismuth Nitrate Solution:

Dissolve 30.0 g of $\text{Bi}(\text{NO}_3)_3$ in 100 mL of D.I. water. While stirring, add 250 mL of concentrated acetic acid. Stir until dissolved. Dilute to 1 liter with D.I. water.

6. Sulfamic Acid Solution: Dissolve 40.0 g of sulfamic acid in D.I. water. Dilute to 1 liter.

Notes:

1. CAUTION: Use care in handling of samples with cyanide because of the toxicity. Avoid skin contact, inhalation, or ingestion. ALWAYS HAVE A RESPIRATOR IN AREA WHEN DOING THIS TEST.

If a sample begins to bump or back up the tube, quickly increase the flow rate, and turn the heat down (or off) until bumping subsides.

If a sample does boil over, proceed as follows:

- Put on respirator
 - Turn heat off (For your protection, use gloves.)
 - Pull inlet tube out
 - Put sample and heating mantle into hood
 - When sample is cool remove from mantle and heat mantle in hood on high until acid fumes have dissipated.
2. Oxidizing agents, such as chlorine, interfere by decomposing cyanides. If chlorine is believed to present, put a drop of sample on potassium iodide starch paper. If paper turns bluish, add a few crystals of sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$) to the sample, mix, and retest. Continue adding sodium thiosulfate until free from chlorine. Then, add 0.1 g sodium thiosulfate in excess.
 3. Sulfides interfere by forming thiocyanate at a high pH. If sulfides are believed to be present, put a drop of sample on lead acetate test paper treated with acetic acid buffer solution at pH4. Darkening of paper indicates sulfides. If sulfides are present, add 50 mL of bismuth nitrate solution after the air rate is set through the air inlet tube. Mix for 3 minutes prior to addition of H_2SO_4 . Alternatively, $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, CdCO_3 or PbCO_3 can be added after the distillation, but prior to color development. Bismuth nitrate added prior to the distillation process is the preferred choice.
 4. Fatty acids, high carbonates, and aldehydes can interfere. Refer to Standard Methods for troubleshooting.

5. High concentrations of NO_3 and NO_2 can give false positive results. If samples contain high concentrations of NO_3 and/or NO_2 , add 50 mL of sulfamic acid solution after the air rate is set through the air inlet tube. Mix for 3 minutes prior to addition of H_2SO_4 .

Procedure:

1. All glassware is to be soap and water washed, tap rinsed, and deionized rinsed prior to analyses. Dichromate or acetone may also be used to clean the glassware prior to the soap and water wash.
2. Connect and set up cyanide reflux distillation apparatus as shown in Figure 2.
3. Prepare the 0.10 mg/L cyanide calibration standard as follows:
Add 5 mL of the 5 mg/L cyanide solution to 250 mL of DI water.
(Prepare in the distillation flask.)
4. Pour 250 mL of sample into cyanide distilling flask. If a solid or semi-solid sample is to be analyzed, use a 1.0 g sample size and add 250 mL of D.I. water to the distilling flask. (Record the amount of sample used.) Add an additional 250 mL D.I. water for a total volume of 500 mL in the distillation flask.

To Spike: Add 5 mL of the 5 mg/L cyanide solution to the 250 mL of sample, for a final concentration of 0.10 mg/L CN.
5. Using a graduated cylinder, add 50 mL 1.25 N sodium hydroxide to the absorber tube and connect.
6. Turn on vacuum pump and adjust so that one bubble per second enters the distillation flask through the air inlet tube.
7. Slowly add 25 mL concentrated sulfuric acid through the air inlet tube. Rinse the tube with D.I. water and wait for about 2-3 minutes, until the sulfuric acid has been dispersed into the sample.
8. Using a graduated cylinder, add 20 mL magnesium chloride solution into the air inlet tube and rinse the tube with D.I. water.
9. Turn heating mantle on to 60-63% of scale. Watch vacuum rate carefully and adjust as necessary maintaining a rate of one bubble per second. As the temperature increases, bubbling increases, and the solution can be drawn from the absorption tube or blown out the air inlet tube. Reflux for one hour after the sample comes to a boil.
10. Turn off heat and continue vacuum for 15 minutes.
11. Disconnect absorber, DI rinse absorber top into absorbing solution, and shut off vacuum pump.

12. Pour solution from absorber tube into a 250 mL volumetric flask. Using D.I. water, rinse the absorption tube (3 times) and add to the volumetric flask. Dilute to mark with DI water. Mix by inverting.
13. Distillates are ready for analysis. Proceed with Lachat SOP CNAHC for the automated colorimetric step.

Quality Control:

1. The standard curve does not need to be carried through the distillation procedure.
2. A reagent blank is to be analyzed with each set of samples. This blank is to be carried through the distillation steps as a check for contamination. Date and initial blank container.
3. A quality control calibration standard of 0.10 mg/L cyanide is to be analyzed with each set of samples. This standard is to be carried through the entire procedure including the distillation step. This standard must be within 90-110 % of the true value, or the samples are to be reanalyzed. Date and initial standard container.
4. A known reference standard (LCS) is to be analyzed with each set of samples. This standard is to be carried through the entire procedure including the distillation steps. This standard must be within 80-120 % of the true value and within 95% confidence limits (if available) or the samples are to be reanalyzed.
5. Duplicate and spike a minimum of 1 out of 10 samples. If less than 10 samples are analyzed, a duplicate and spike are still required. Spike recoveries and duplicate results are to be within acceptable ranges.
6. Aqueous and solid/semi-solid samples are separate matrices. Duplicates and spikes are required for each matrix type.

Calculation:

1. Calculate with Lachat QuikChem software, in the concentration mode, using the IBM XT computer. (Be sure to calculate in any distillation dilution into the final result.)

TOTAL CYANIDE - AUTOANALYZER - (HEATED METHOD)

Scope and Application: This method is applicable to distilled groundwater, drinking water, wastewater, sediments and soils. All samples must be distilled prior to analysis with the autoanalyzer. (Refer to SOP # CNDISC.)

Reference: EPA, 1983, Method 335.3
Lachat Instruments, 1986, Method 10-204-00-1-A
Standard Methods, 16th Edition, pages 337-338

Instrument Detection Limit: 0.005 mg/L

Optimum Concentration Range: 0.005 - 0.40 mg/L

Sample Handling: Samples should be capped and refrigerated at 43C after distillation. Read no later than 7 days after distillation.

Instrument Conditions:

1. Pump speed: 35
2. Cycle period: 50 seconds
3. Load period: 20 seconds
4. Inject period: 15 seconds
5. Inject to start of peak period: 30 seconds
6. Inject to end of peak period: 78 seconds
7. Gain: 420
8. Zero: 350
9. Interference filter: 570 nm
10. Sample loop: 150 cm (0.80 mm i.d.)
11. Standards for calibration: 0, 0.02, 0.04, 0.10, 0.20, 0.40 mg/L
12. Water Bath 453C (Position A).

Reagent Preparation: (Prepare fresh every 6 months unless otherwise noted.)

1. Degassed Milli-Q-water - 2 options:

- a. Boil Milli-Q water vigorously for 5 minutes. Cool and store in cubitainer.
- b. Bubble helium, using the fritted gas dispersion tube, through 20 L Milli-Q water for 15-20 minutes. Store in cubitainer.

2. Carrier - 0.25N NaOH:

In a 1 L volumetric flask, dissolve 10.0 g NaOH in 900 mL DI water. Dilute to the mark and invert several times. Filter through 0.45 micron filter paper. Store in a plastic bottle.

3. Phosphate Buffer - 0.86M (pH 5.2):

In a 1 L volumetric flask, dissolve 97.0 g KH_2PO_4 in 800 mL degassed MQ water. Add 8.1 mL concentrated (85%) phosphoric acid. Dilute to the mark with degassed MQ water and invert several times.

4. Chloramine-T Solution:

In a 500 ml volumetric dissolve 2.0 g of chloramine-T in degassed Milli-Q. Dilute to the mark and invert several times. Prepare fresh weekly and store refrigerated.

5. Pyridine - Barbituric Acid Reagent:

In the fume hood, place 15.0 g barbituric acid in a 1 L beaker and add 100 mL of degassed MQ water, rinsing down the sides of the beaker to wet the barbituric acid. Add 75 mL pyridine ($\text{C}_5\text{H}_5\text{N}$) while stirring with stir bar. Mix until barbituric acid dissolves. Add 15 mL concentrated HCl and stir. Transfer to a 1 L volumetric flask, dilute to the mark with degassed MQ water and invert several times. Refrigerate. Prepare fresh every 2 months.

6. Stock Cyanide Solution (1000 mg/L):

Dissolve 0.6275 g KCN and 0.5 g KOH and dilute to 250 mL with D.I. water in a volumetric flask. Prepare fresh every month. Refrigerate.
CAUTION: TOXIC!

7. Standard Cyanide Solution (5.0 mg/L):

Pipet 5 mL of stock cyanide solution into 1 L volumetric flask, add approximately 500 mL DI water. Add 2 mL of 10N NaOH as a preservative and dilute to volume with DI water. Prepare fresh weekly. Refrigerate.

8. Cyanide Standards:

Prepare by pipetting the volumes noted below into 250 mL volumetric flasks, adding 50 mL of 1.25N NaOH, and diluting to the mark with degassed MQ water. (The 1.25N NaOH must be added - very important!) Prepare fresh weekly. (7 days)

<u>Concentration of Standard</u>	<u>Letter Identifier</u>	<u>Volume of 5 mg/L working standard (ml)</u>
0.00 mg/L	A	0 mL
0.02 mg/L	B	1.0 mL
0.04 mg/L	C	2.0 mL
0.10 mg/L	D	5.0 mL
0.20 mg/L	E	10 mL
0.40 mg/L	F	20 mL

Note: Computer refers to standards by letter.

NOTES:

1. This chemistry is temperature sensitive. The heated method reduces or eliminates sensitivity drift due to temperature changes.
2. Use wasteline coil to help eliminate air spikes.
3. Any sample dilutions must be diluted with 0.25N NaOH, not water. You may use the carrier or the zero standard for this.
4. Interferences are reduced or eliminated by the distillation procedure. Cyanide analyses suffer from many interferences. See EPA and Standard Methods references for detailed discussion. Information and recommendations for the manual pyridine-barbituric acid color development also apply to this automated method.
5. Samples must be diluted to obtain concentrations within the optimum working range.
6. The gain and zero settings are guidelines and must be adjusted each day to optimize.
7. Color is an interference, dilute the sample and also manually spike the dilution to confirm the quality of the result.

System Operation:

1. Refer to "Auto Analyzer Operation Start-up Procedure" (IOP # LAA - Section A).
2. Spikes will be distilled at a level of 0.10 mg/L. The calibration check standard is 0.10 mg/L.
3. Analyze a calibration check standard, blank, and known reference standard at the beginning of each run. All standards must be within required control limits before any samples are analyzed.
4. Refer to Auto Analyzer shut-down procedure. (IOP # LAA - Section B).

Quality Control:

1. Establish a standard curve with the standards listed above. The derived concentrations for each calibration standard must read within 10% of the true value.

2. A quality control calibration standard (0.10 mg/L) and blank are to be analyzed initially and at a minimum, after every 10 samples. If less than 10 samples are analyzed, a calibration standard and blank are still required. The last samples analyzed in the run are to be the calibration standard and blank. These standards must be within the acceptable ranges or the samples run after the last acceptable check standard are to be reanalyzed.
3. Duplicate and spike a minimum of 1 out of 10 samples. If less than 10 samples are analyzed, a duplicate and spike are still required. Spike recoveries and duplicates are to be within acceptable ranges or data must be flagged appropriately. (These samples must be carried through the distillation step.)

Calculations:

1. Calculate with Lachat QuikChem software, in the concentration mode, using the IBM XT computer. Be sure to calculate any digestion dilution into the final result.

TOTAL MERCURY
Liquid Samples

Scope and Application: This method is applicable to drinking, surface, groundwater, domestic, and industrial wastewaters.

Method: Manual Cold Vapor

Reference: EPA 1983, Method 245.1

Detection Limits: 0.0002 mg/L (in 100 mL sample)

Optimum Range: 0.0002-0.010 mg/L

Sample Handling: Preserve with concentrated HNO_3 to pH <2. Analyze within 28 days of sampling.

Reagents and Apparatus:

1. Mercury cold-vapor Analyzer System
2. Water bath set @ 95°C
3. BOD bottles; 300 mL
4. Class A volumetric glassware
5. Instra-Analyzed sulfuric acid
6. Instra-analyzed nitric acid
7. Potassium persulfate
8. Potassium permanganate
9. Sodium chloride
10. Hydroxylamine hydrochloride solution
11. Stannous chloride
12. Various Class A volumetric pipettes
13. Mercury lamp
14. Mercury stock and standard solutions
15. Drierite
16. Activated charcoal
17. Glass wool
18. Tygon tubing

Reagent Preparation: (Prepare fresh every 6 months, unless otherwise noted.)

1. Sulfuric acid (0.5 N): Pipet 14.0 mL of conc. H_2SO_4 to 500 mL D.I. water in a 1 liter volumetric flask, dilute to the mark. PREPARE IN THE HOOD!
2. Stannous chloride (10% w/v): Add 100.0 g stannous chloride to 1 liter of 0.5 N sulfuric acid.

3. Sodium chloride-hydroxylamine hydrochloride solution: Dissolve 120.0 g of sodium chloride and 120.0 g of hydroxylamine hydrochloride in D.I. water, dilute to 1 liter.
4. Potassium permanganate (5% solution, w/v): Dissolve 50.0 g of potassium permanganate in D.I. water, dilute to 1 liter.
5. Potassium persulfate (5% solution, w/v): Dissolve 50.0 g of potassium persulfate in D.I. water, dilute to 1 liter.
6. Intermediate mercury standard (10.0 mg/L): Transfer 1.0 mL stock mercury (1000 mg/L) solution, plus 1/2 mL nitric acid, into a 100 mL volumetric flask and dilute to the mark with D.I. water. Prepare fresh daily!
7. Working mercury standard (0.100 mg/L): Transfer 1.0 mL of the 10.0 mg/L intermediate standard, plus 1/2 mL nitric acid, into a 100 mL volumetric flask and dilute to the mark with D.I. water. Prepare fresh daily!

Notes:

1. The mercury standards are volatile and unstable. Standards must be prepared daily.
2. Because of the toxic nature of mercury vapor, precaution must be taken to avoid inhalation. Vent the mercury vapor into an exhaust hood or pass the vapor through an absorbing media.
3. A 10% solution of stannous sulfate may be substituted for stannous chloride.
4. Hydroxylamine sulfate may be used rather than hydroxylamine hydrochloride.
5. Standard additions must be used for all EP extracts and delisting petitions.
6. The calibration check standard is a 0.005 mg/L standard.
7. Interferences:
 - a. Potassium permanganate is added to eliminate interferences from sulfide. Concentrations as high as 20 mg/L sulfide as sodium sulfide do not interfere.
 - b. Copper has also been reported to interfere; however, copper concentrations as high as 10 mg/L have no effect on recovery of mercury from spiked samples.

- c. Seawaters, brines, and industrial effluents, high in chlorides, will require additional potassium permanganate. during the oxidation step, chlorides are converted to free chlorine which also absorbs at the same wavelength as mercury. Care must be taken to ensure that free chlorine is absent before the mercury is reduced and swept into the cell. this may be accomplished by using an excess of hydroxylamine chloride reagent. In addition, the dead air space in the BOD bottle must be purged before adding the stannous sulfate.
- d. Certain volatile organic materials that absorb at this wavelength may also cause an interference. A preliminary run without reagents should determine if this type of interference is present.

Instrument Conditions:

1. Wavelength: 253.6 nm. Background is required.
2. Slit Width: 0.7
3. Mode: Absorbance
4. Time = 40 seconds
5. Standards to use for curve set-up: 0.5, 1.0, 5.0, 10.0 ug/L.

Cold Vapor System Set-up:

Cell Alignment:

1. Insert quart cell in burner chamber. (Replace the burner head in the burner chamber.)
2. Align cell in light path (use 0.5 sec t, adjust to the lowest abs. reading).
3. Check drying tube and charcoal tube - replace if necessary (see attached page).
4. Insert aerator into a BOD bottle filled with 100 mLs D.I. water.
5. Turn on pump.
6. Let warm-up a few minutes.
7. Zero machine.

Procedure:

All glassware is to be washed with soap and water, rinsed with tap water, acid rinsed with 10% HNO_3 , and final rinsed with D.I. water.

A. Standard Preparation

1. The standard curve is to consist of the following standards:

Standard
Concentration

0.00 ug/L
0.50 ug/L
1.00 ug/L
5.00 ug/L
10.0 ug/L

2. Pipet 0, 0.5, 1.0, 5.0, and 10.0 mL aliquots of 0.10 ug/mL working stock mercury solution to 300 mL BOD bottles.
3. Add D.I. water to bring volume to 100 mL and continue with the digestion procedure.

B. Sample Preparation:

1. Transfer 100 mL, or an aliquot diluted to 100 mL, to a 300 mL BOD bottle.

To Spike: Pipette 5.0 mL of 0.10 mg/L standard into the sample bottle. Proceed as written.

C. Digestion:

1. Add 5 mL conc. sulfuric acid and 2.5 mL conc. nitric acid to each bottle. Mix by swirling.
2. Add 15 mL potassium permanganate solution to each bottle, mix by swirling. Allow to stand for at least 15 minutes. If the bottle does not remain purple in color, additional potassium permanganate is required.
3. Add 8 mL of potassium persulfate solution to each bottle and heat for 2 hours in a water bath maintained at 95°C. Check the bottles periodically throughout the 2 hours to insure the samples remain purple. Add potassium permanganate if needed.
4. Cool to room temperature.

D. Sample Analysis:

1. Add 6 mL of sodium chloride-hydroxylamine hydrochloride solution to reduce excess permanganate. If necessary, additional amounts of sodium chloride hydroxylamine hydrochloride may be required to discharge the purple color. Swirl.
2. Add 5 mL of stannous chloride solution and immediately insert the aerator, making sure that the stopper provides a good seal.
3. Press the read button.
4. Record the absorbance value on the bench sheet.
5. Remove the aerator, rinse aerator, and place it in the D.I. blank bottle.
6. Repeat for additional samples.

Quality Control:

1. Establish a standard curve with the standards listed above plus a blank. Record the absorbance check standard in the absorbance check book. The absorbances should remain consistent from run to run. If not, necessary troubleshooting must be performed before continuing (check wavelength, tubing, lamp alignment, pump, etc.)
2. A quality control calibration standard of 0.005 mg/L and a blank are to be analyzed initially, and after every 10 samples. These standards are to be carried through the digestion procedure. If less than 10 samples are analyzed, a calibration standard and a blank are still required. The last samples analyzed in the run are to be the calibration standard and blank. These standards must be within acceptable ranges or the samples run after the last acceptable calibration standard are to be reanalyzed. Record the calibration standard in the quality control book. The confidence limits are noted in the quality control book.
3. Duplicate and spike a minimum of 1 out of 10 samples. If less than 10 samples are analyzed, a duplicate and spike are still required. Spike recoveries and duplicate results are to be within acceptable ranges or the data must be flagged appropriately.

Calculation:

1. Calculate using linear regression.

Calculate the spike recovery as follows:

$$\% \text{ Recovery} = \frac{(\text{ug/L spiked sample}) - (\text{ug/L sample})}{5.0 \text{ ug/L}} \times 100$$

MERCURY MANUAL COLD VAPOR TECHNIQUE

Solid and Semi-Solid Samples

Scope and Application: This procedure is applicable for determining total mercury (organic, inorganic) in soils, sediments, and sludge-type samples. All samples must be subjected to a digestion step prior to analysis.

Method: Mercury - Cold Vapor

Reference: EPA, 1983, Method 245.5

SW846, 1982, Method 7471

Detection Limit: 0.04 mg/kg (if 0.5 gm sample aliquots are used)

Sample Handling: Due to the extreme sensitivity of this procedure, sampling devices and containers should be free from mercury. Soils are analyzed as received. The sample should be crushed and thoroughly mixed before the sample is weighed for analysis.

Reagents and Apparatus: (All glassware is acid washed and rinsed three times with D.I. water.) Use D.I. water only.

1. Mercury cold-vapor analyzer system
2. Mercury lamp
3. Instra-Analyzed nitric acid
4. Instra-Analyzed hydrochloric acid
5. Mercury stock and standard solutions
6. Class A volumetric glassware
7. Deionized Water
8. Water bath set at 95 C
9. 300 mL BOD bottles
10. Instra-Analyzed sulfuric acid
11. Stannous chloride
12. Sodium chloride
13. Hydroxylamine hydrochloride
14. Potassium permanganate
15. Drierite
16. Activated charcoal
17. Glass wool
18. Tygon tubing

Reagent Preparation: (Prepare fresh every 6 months, unless otherwise stated.)

1. Aqua - Regia: PREPARE IMMEDIATELY before use! PREPARE IN THE HOOD!
3 Volumes conc. HCL + 1 volume conc. HNO₃
2. 0.5N H₂SO₄ - Dilute 14.0 mL of conc. H₂SO₄ to 1 liter with D.I. water.
PREPARE IN THE HOOD!
3. Stannous Chloride: Add 100.0g stannous chloride to 1 L of 0.5N H₂SO₄.
4. Sodium chloride - hydroxylamine hydrochloride solutions: Dissolve 120.0 grams NaCl + 120.0 grams hydroxylamine hydrochloride in approximately 100 mL D.I. water, dilute to 1 liter with D.I. water.

5. Potassium permanganate 5% solution: Dissolve 50.0g potassium permanganate in D.I. water and dilute to 1 liter with D.I. water.
6. Potassium persulfate (5% solution, w/v): Dissolve 50.0 g of potassium persulfate in D.I. water, dilute to 1 liter.
7. Intermediate mercury standard (10.0 mg/L): Transfer 1 mL stock mercury (1000 mg/L) solution, plus 1/2 mL concentrated nitric acid, into a 100 mL volumetric flask and dilute to the mark with D.I. water. Prepare fresh daily!
8. Working mercury standard (0.100 mg/L): Transfer 1.0 mL of the 10.0 mg/L intermediate standard, plus 1/2 mL concentrated nitric acid, into a 100 mL volumetric flask and dilute to the mark with D.I. water. Prepare fresh daily!

Notes:

1. Mercury is volatile and unstable; therefore intermediate and working standards must be prepared daily.
2. Because of the toxic nature of mercury vapor, precaution must be taken to avoid inhalation. Vent the mercury vapor into an exhaust hood or pass the vapor through an absorbing media.
3. Rinse aerator off with DI water between sample. When rinsing, be careful not to rinse too high on the aerator, otherwise the pump will suck the water into the analyzer.
4. A 10% solution of stannous sulfate maybe substituted for stannous chloride.
5. Hydroxylamine sulfate may be used rather than hydroxylamine hydrochloride.
6. Interferences:
 - A. Potassium permanganate is added to eliminate possible interference from sulfide. Concentrations as high as 20 mg/L sulfide as a sodium sulfide do not interfere.
 - B. Copper has also been reported to interfere; however, copper concentrations as high as 10 mg/L have no effect on recovery of mercury from spiked samples.
 - C. Seawaters, brines, and industrial effluents high in chlorides require additional potassium permanganate. During the oxidation step, chlorides are converted to free chlorine which also absorbs at the same wavelength as mercury. Care must be taken to ensure that free chlorine is absent before the mercury is reduced and swept into the cell. This may be accomplished by using an excess of hydroxylamine sulfate reagent. In addition, the dead air space in the BOD bottle must be purged before adding stannous sulfate.

- D. Certain volatile organic materials that absorb at this wavelength may also cause an interference. A preliminary run without reagents should determine if this type of interference is present.

Instrument Conditions:

1. Wavelength: 253.6 nm. Background is required.
2. Slit Width: 0.7
3. Mode: Absorbance
4. Time = 40 seconds
5. Standards to use for curve set-up: 0.5, 1.0, 5.0, 10.0 ug/L.

Cold Vapor System Set-Up:

Cell Alignment:

1. Insert quart cell in burner chamber. (Replace the burner head in the burner chamber.)
2. Align cell in light path (use 0.5 sec t, adjust to the lowest abs. reading).
3. Check drying tube and charcoal tube - replace if necessary (see attached page).
4. Insert aerator into a BOD bottle filled with 100 mLs D.I. water.
5. Turn on pump.
6. Let warm-up a few minutes.
7. Zero machine.

Procedure:

A. Standard Preparation:

1. The standard curve is to consist of the following standards:
D.I. water blank
0.50 ug/L
1.0 ug/L
5.0 ug/L
10.0 ug/L
2. Prepare the standards above by pipetting 0, 0.5, 1.0, 5.0, and 10.0 mL aliquots of 0.10 ug/mL working mercury solution to 300 mL BOD bottles.
3. Add D.I. water to bring volume up to 10 mL, and continue with the digestion procedure.

B. Sample Preparation

1. Weigh 0.50 gram of sample and place in the bottom of a BOD bottle. Record the weight used.

To Spike: Pipet 1.0 mL of 0.10 ug/L standard into sample bottle.

2. Add 10 mL of D.I. water, and continue with the digestion procedure.

C. Digestion

To all samples, standards, and blanks:

1. Add 5 mL aqua regia solution, cap bottles.
2. Heat 2 min. in a water bath at 95 C. (Waterbath must be maintained at 95 C).
3. Cool, add 50 mL D.I. water.
4. Add 30 mL potassium permanganate solution.
5. Add 8 mL of potassium persulfate.
6. Mix thoroughly and place in a water bath at 95 C for 30 minutes. Check samples periodically throughout the 30 minutes to insure they are purple in color. If not, add potassium permanganate. Add the same volume of potassium permagnate to all bottles.
7. Cool samples and standards to room temperature.
8. Add 50 mL of D.I. water.

D. Sample Analysis:

1. Add 6 mL sodium chloride-hydroxylamine hydrochloride to reduce the excess permanganate. Additional sodium chloride-hydroxylamine hydrochloride may be needed to discharge the purple color. Swirl.
2. Add 5 mL of stannous chloride solution and immediately insert the aerator, making sure that the stopper provides a good seal.
3. Press the read button.
4. Record the absorbance reading.
5. Remove the aerator, rinse aerator, and place into the D.I. blank bottle.
6. Repeat for additional samples.

Quality Control

1. Establish a standard curve with the standards listed above plus a blank. Record the absorbance check standard in the absorbance check book. The absorbances should remain consistent from run to run. If not, necessary troubleshooting must be performed before continuing (check wavelength, tubing, lamp alignment, pump, etc.,)
2. A quality control calibration standard of 0.005 mg/L and a blank are to be analyzed initially, and after every 10 samples. If less than 10 samples are analyzed, a calibration standard and blank are still required. The last samples analyzed in the run are to be the calibration standard and blank. These standards must be within acceptable ranges or the samples run after the last acceptable calibration standard are to be reanalyzed.
3. Duplicate and spike a minimum of 1 out of 10 samples. If less than 10 samples are analyzed, a spike and duplicate are still required. Spike recoveries and duplicate results are to be within acceptable ranges or the data must be flagged accordingly.

Calculation:

1. Calculate using linear regression (absorbance vs. concentration).

$$\text{mg/kg Mercury} = \frac{(\text{mg/L sample}) (100 \text{ mL})}{\text{grams of sample}}$$

Calculate the spike recovery as follows:

$$\% \text{ Recovery} = \frac{(\text{mg/kg spiked sample}) - (\text{mg/kg sample})}{(5.0 \text{ ug}) / (\text{grams of spiked sample})} \times 100$$

AMMONIA NITROGEN

Scope and Application: This method is applicable to the determination of ammonia-nitrogen in drinking water, surface water, groundwater, sludges, soils, and industrial wastes.

Method: Micro-distillation, Colorimetric

Reference: EPA, 1983, Method 350.2

Detection Limit: 0.10 mg/L for aqueous samples
5.00 mg/kg for soils and sludges

Optimum Range: 0.10 - 2.00 mg/L for aqueous samples
5.00 - 100 mg/kg for soils and sludges

Sample Handling: Acidify aqueous samples with concentrated sulfuric acid to pH <2 and refrigerate at 4°C. Refrigerate soils and sludges at 4°C. Analyze within 28 days of sampling.

Reagents and Apparatus:

1. Kjeldahl flasks, 100 mL
2. Keeney distillation apparatus
3. Spectrophotometer, set at 425nm with sipper cell
4. Erlenmeyer flasks, 50 mL
5. Sulfuric acid, concentrated
6. Milli-Q water
7. pH meter, 0.1 pH unit sensitivity
8. Volumetric glassware, Class A (pipets and flasks)
9. Top loading balance, 0.01g sensitivity
10. Graduated cylinders, 50 mL
11. Mixing cylinders, 50 mL
12. Ammonium chloride (NH_4Cl)
13. Boric acid (H_3BO_3)
14. Mercuric iodide (HgI_2)
15. Potassium iodide (KI)
16. Sodium hydroxide (NaOH)
17. Sodium tetraborate ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$)
18. Sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$)
19. Analytical balance, 0.0001g sensitivity
20. 150 mL beaker
21. Stir bars and stir plate

Reagent Preparation: (Prepare fresh every 6 months, unless otherwise stated).

1. Ammonium chloride stock solution(1000 mg/L): In a 1 liter volumetric flask, dissolve 3.819g NH_4Cl in approximately 300 mL Milli-Q water and bring to volume. Preserve with H_2SO_4 to a pH<2. Refrigerate.

2. Ammonium chloride standard solution (10 mg/L): Dilute 10.0 mL of the ammonium chloride stock solution to 1 liter with Milli-Q water in a volumetric flask. Preserve with H_2SO_4 to a $\text{pH} < 2$. Prepare monthly. Refrigerate.
3. Boric acid solution: Dissolve 20.0g H_3BO_3 in Milli-Q water and dilute to 1 liter in a volumetric flask.
4. Nessler reagent: Dissolve 100g of mercuric iodide and 70g of potassium iodide in about 200 mL of Milli-Q water. Add this mixture slowly, while stirring to a COOLED solution of 160g NaOH in 500 mL Milli-Q water. Dilute the mixture to 1 liter. Store in a Pyrex bottle and keep out of direct sunlight. (refrigerate) NOTE: Commercially available.
5. Sodium hydroxide (1N): Dissolve 40g of NaOH in Milli-Q water and dilute to 1 liter.
6. Sodium hydroxide (0.1N): Dilute 100 mL of 1N NaOH to 1 liter with Milli-Q water.
7. Sodium tetraborate solution (0.025M): Dissolve 9.5g of $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ or 5.0g anhydrous $\text{Na}_2\text{B}_4\text{O}_7$ in Milli-Q water and dilute to 1 liter.
8. Borate buffer: Add 88 mL of 0.1N NaOH solution to 500 mL of 0.025M sodium tetraborate solution. Dilute to 1 liter with Milli-Q water.
9. Sodium thiosulfate (1/70N): Dissolve 3.5g $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ in Milli-Q water and dilute to 1 liter. (1 mL of this solution will remove 1 mg/L of residual chlorine in 500 mL of sample).

NOTES:

1. Residual chlorine must be removed prior to distillation by pretreating the sample with sodium thiosulfate solution.
2. Pre-steam the distillation apparatus with 10% NaOH before use, for each batch analyzed.
3. Cyanate and some volatile alkaline compounds may cause an offcolor nesslerization. This off-color can be eliminated by boiling the sample at a low pH (pH 2-3) to drive off the compound. This should be done prior to the distillation step.

Procedure: Sample must be homogenized prior to analysis to ensure a representative sample aliquot.

Distillation:

1. All glassware is to be soap and water washed, tap water rinsed, and Milli-Q water rinsed prior to use.

2. The reservoir should be 2/3 full with Milli-Q water. Add a few boiling chips. Add sulfuric acid to reservoir to bring to a pH <2. Turn on the heater. Set heater control to HIGH. Allow the steam reservoir to heat up. This unit will take about 45 minutes to heat-up. Turn the heater control to about a setting of 8 and bring to boiling. Analysis can begin once boiling begins.
3. Prepare the distillation apparatus as follows: Steam out the distillation apparatus with a 10% NaOH solution. Turn on water and continue until 40 mL has been distilled.
4. Aqueous samples:
Place 50 mL or an aliquot of sample diluted to 50 mL in a 150 mL beaker. Record the volume used. Add 1N NaOH while stirring very slowly until the pH is 9.5 ± 0.1 using pH meter.
To spike: Place 50 mL sample and 5 mL of the 10 mg/L ammonia standard into a beaker, adjust pH to 9.5 ± 0.1 and continue with procedure. Final spike level is 1.0 mg/L.
Non-aqueous samples:
Place approximately 1.0g in a 150 mL beaker. Record weight used. Add 50 mL Milli-Q water and adjust the pH with 1N NaOH, while stirring slowly, to pH 9.5 ± 0.1 using pH meter.
To spike: Place 1.0g sample, 5 mL of the 10 mg/L ammonia standard in the beaker. Add 50 mL Milli-Q water, adjust pH, and continue with procedure.
5. Transfer the pH-adjusted sample to a 100 mL Kjeldahl flask. Add 2.5 mL of borate buffer.
6. Add 5 mL of boric acid to a 50 mL Erlenmeyer flask and place flask at the condenser outlet with the tip of the condenser immersed in the boric acid.
7. Connect the Kjeldahl flask to the distillation apparatus and secure with springs.
8. Close the stopcock on the condensation chamber. Close the drain stopcock. The steam will now pass through the Kjeldahl flask.
9. Steam distill 30-40 mL at a rate of 4-5 mL/min.
10. Rinse tip of condenser into erlenmeyer flask, remove the erlenmeyer flask.
11. Rinse the tip of the condenser and steam outlet into a waste beaker.

12. Continue distilling remaining samples, blanks and standards. When all samples, blanks and standards are distilled, the colorimetric determination can be performed.

Colorimetric Determination:

1. Prepare the following series of blanks and standards in 50 mL mixing cylinders containing 5 mLs of boric acid solution (These do not need to be taken through the distillation step).

<u>mL of 10 mg/L ammonium chloride solution</u>	<u>Dilute to</u>	<u>Concentration (mg/L)</u>
0	50 mL	BLANK
0.5	50 mL	0.10
1.0	50 mL	0.20
2.0	50 mL	0.40
5.0	50 mL	1.00
10.0	50 mL	2.00

2. Add 2.0 mL of Nessler reagent to the blank and standards. Stopper and mix by inverting several times.
3. After 20 minutes, read the absorbances on the spectrophotometer set at 425nm using the sipper cell. Zero the spectrophotometer to the reagent blank.
4. Transfer distilled samples to 50 mL mixing cylinders and dilute to 50 mL with Milli-Q water. Mix.
5. Determine the ammonia in the distillate as follows:
 - Transfer 25 mL of distillate, or an aliquot diluted to 25 mL, to a mixing cylinder.
 - Add 1 mL of Nessler reagent and mix by inverting several times.
 - After 20 minutes, read the absorbance as described in Step 3.

Calculations:

1. Aqueous Samples:
 - a. Calculate using linear regression.
 - b. Multiply in any dilution factors performed in the distillation and colorimetric steps to obtain the final result in mg/L.

2. Non-Aqueous Samples:

- a. Calculate using regression to obtain a mg/L value.
- b. Multiply in any dilution factor performed in the colorimetric step (mg/L).
- c. Multiply result obtained from "Step b" by 50 and divide by grams of sample used to obtain the final result in mg/kg.

Quality Control:

1. Establish a standard curve with the standards listed above plus a blank. Record the absorbance check standards (1.00 mg/L) in the absorbance check book. The absorbances should remain consistent from run to run. If not, necessary troubleshooting must be performed before continuing (check wavelength, spectrometer bulb, solutions, etc.).
2. A distilled blank, standard (1.00 mg/L), and known reference standard are to be analyzed at the beginning of the analytical run. The standards must be within acceptable ranges and the blank less than the detection limit, or troubleshooting must be performed.
3. A quality control calibration standard of 1.00 mg/L and a blank are to be analyzed, initially and after every 10 samples. This standard does not need be carried through the distillation procedure. The last samples analyzed in the run are to be the calibration standard and blank. These standards must be within the acceptable ranges ($\pm 10\%$ of the true value) or the samples run after the last acceptable check standard are to be reanalyzed.
4. Duplicate and spike a minimum of 1 out of 10 samples. If less than 10 samples are analyzed, a duplicate and spike are still required. Spike recoveries and duplicate results are to be within acceptable ranges, or data must be flagged appropriately.

TOTAL KJELDAHL NITROGEN

Scope and Application: This method is applicable for the determination of total kjeldahl nitrogen in drinking water, surface water, groundwater, domestic and industrial wastewaters. Soils, sludges and solid waste samples may also be analyzed by this method.

Method: Micro-digestion, micro-distillation, colorimetric

Reference: EPA 1983, Method 351.3.

Detection Limit: 0.10 mg/L or aqueous samples
5.00 mg/kg for non-aqueous samples

Sample Handling: Acidify aqueous samples with concentrated H_2SO_4 to pH <2 and refrigerate at 4°C. (Non-aqueous samples should be refrigerated at 4°C.) Analyze samples within 28 days of collection.

Reagents and Apparatus:

1. Mercuric oxide, red (HgO)
2. Sulfuric acid, concentrated (H_2SO_4)
3. Potassium sulfate (K_2SO_4)
4. Sodium hydroxide ($NaOH$)
5. Sodium thiosulfate ($Na_2S_2O_3 \cdot 5H_2O$)
6. Micro kjeldahl digestion apparatus
7. Milli-Q water
8. Boiling chips
9. Volumetric glassware (flasks and pipets)
10. 100 mL Kjeldahl flasks
11. Wide-mouth pipets
12. Graduated cylinders, 50 mL
13. Keeney distillation apparatus
14. Spectrophotometer, set at 425nm with sipper cell
15. Erlenmeyer flasks, 50 mL
16. pH meter, 0.1 pH unit sensitivity
17. Top loading balance, 0.01g sensitivity
18. Mixing cylinders, 50 mL
19. Ammonium chloride (NH_4Cl)
20. Boric acid (H_3BO_3)
21. Mercuric iodide (HgI_2)
22. Potassium iodide (KI)
23. Analytical balance, 0.0001g sensitivity

Reagent Preparation: (Prepare fresh every 6 months, unless otherwise stated.)

1. Mercuric sulfate solution: Dissolve 4.0g red HgO in 25 mL of 1:4 sulfuric acid (5 mL conc. H_2SO_4 :20 mL Milli-Q water) and dilute to 50 mL with Milli-Q water.

2. Digestion solution: Dissolve 133.5g K_2SO_4 in 650 mL Milli-Q water and 200 mL conc. H_2SO_4 . Add 25 mL of mercuric sulfate solution and dilute to 1 liter with Milli-Q water. Store at room temperature in glass to prevent crystallization. If crystals do form, heat slowly, while stirring, to dissolve.
3. Sodium hydroxide-sodium thiosulfate solution: Dissolve 500g NaOH and 25.0g $Na_2S_2O_3 \cdot 5H_2O$ in Milli-Q water and dilute to 1 liter. Caution - solution becomes very hot. Store in a plastic bottle.
4. Ammonium chloride stock solution (1000 mg/L): In a liter volumetric flask, dissolve 3.819g NH_4Cl in approximately 300 mL Milli-Q water and bring to volume.
5. Ammonium chloride standard solution (10 mg/L): In a volumetric flask, dilute 10.0 mL of the ammonium chloride stock solution to 1 liter with Milli-Q water.
6. Boric acid solution: In a volumetric flask, dissolve 20.0g H_3BO_3 in Milli-Q water and dilute to 1 liter.
7. Nessler reagent: Dissolve 100g of mercuric iodide and 70g of potassium iodide in about 200 mL of Milli-Q water. Add this mixture slowly, while stirring to a COOLED solution of 160g NaOH in 500 mL Milli-Q water. Dilute the mixture to 1 liter. Store in a Pyrex bottle and keep out of direct sunlight. Refrigerate. Note: Also commercially available.
8. Sodium hydroxide (1N): Dissolve 40g NaOH in Milli-Q water and dilute to 1 liter.
9. Nicotinic acid stock solution (1000 mg-N/L): Dissolve 8.788g in 900 mL Milli-Q water, add 2 mL H_2SO_4 and dilute to 1 liter.
10. Nicotinic acid standard solution (50 mg-N/L): In a 100 mL volumetric flask, dilute 5.0 mL of the nicotinic acid stock solution to 100 mL with Milli-Q water.

NOTES:

1. High nitrate concentrations (10 times or greater that of the TKN level) result in low TKN values. Dilute samples and spike if nitrate interferences are expected.
2. The distillation unit can occasionally build up with mercury. Wash the distillation unit with 10% HCL to prevent build-up in the tubes.
3. Contamination can be a problem. Be sure to wash all glassware and apparatus thoroughly and rinse with Milli-Q water prior to use.

Procedure: Sample must be homogenized prior to analysis to ensure a representative sample aliquot.

A. Digestion:

1. All glassware must be soap and water washed, tap water rinsed and Milli-Q water rinsed prior to use.
2. Prepare the following series of blanks and standards. These standards are to be taken through the distillation step.

<u>mL of 10 mg/L ammonium chloride solution</u>	<u>Dilute to</u>	<u>Concentration (mg/L)</u>
0	50 mL	BLANK
2.0	50 mL	0.40
5.0	50 mL	1.00
7.0	50 mL	1.40
10.0	50 mL	2.00

3. For aqueous samples: Measure out 50 mL sample (or an aliquot diluted to 50 mL if elevated TKN levels are expected) into a 100 mL Kjeldahl flask. Record the volume used.

To spike aqueous samples: Measure 50 mL sample and 5 mL of the 10 mg/L ammonium chloride standard and proceed.

For non-aqueous samples: Weigh out approximately 1.0g sample into a 100 mL Kjeldahl flask. Record weight used. Add 50 mL Milli-Q water.

To spike non-aqueous samples: Weigh out approximately 1.0g sample, add 5 mL of the 10 mg/L ammonium chloride standard and proceed. Record weight used.

4. Add 10 mL of digestion solution to the kjeldahl flask using a 10 mL wide-mouth pipet. Add 3-5 boiling chips.
5. Place flask on micro Kjeldahl digestion apparatus and digest until dense, white SO₃ fumes are given off and the solution turns colorless or straw yellow. Digestion must be performed in the hood! Digest the samples with the digestion apparatus set at 3-4.
6. Digest for 30 minutes more.
7. Cool and add 30 mL Milli-Q water. Cap with parafilm if not distilling immediately.
8. Proceed to the distillation portion of the procedure.

B. Distillation:

1. All glassware is to be soap and water washed, tap water rinsed, and Milli-Q water rinsed prior to use.
2. The reservoir should be 2/3 full with Milli-Q water. Add a few boiling chips. Add sulfuric acid to reservoir to bring to a pH <2. Turn on the heater. Set heater control to HIGH. Allow the steam reservoir to heat up. This will take about 45 minutes. Turn the heater control to about a setting of 8 and bring to boiling. Analysis can begin once water is boiling.
3. Preparation of the distillation apparatus: Steam out the distillation apparatus with a 10% NaOH solution. Analyze a blank to confirm no trace of ammonia exists (no color change with the addition of Nessler reagent to the distillate).
4. Add 5 mL of boric acid to a 50 mL Erlenmeyer flask and place at the condenser outlet with the tip of the condenser immersed in the boric acid.
5. Connect the Kjeldahl flask to the distillation apparatus and secure with springs.
6. Fill the NaOH chamber to the 10 mL mark with NaOH/thiosulfate solution. Slowly lift glass stopper to allow solution to run down tube and into sample distillation flask. Stop flow if "neutralizing action" becomes too vigorous or siphoning back of receiving solution occurs. Replace glass stopper in chamber.
7. Close the stopcock on the condensation chamber. Close the drain stopcock. The steam will now pass through the Kjeldahl flask.
8. Steam distill 30-40 mL at a rate of 4-5 mL/min.
9. Rinse tip of condenser with Milli-Q into erlenmeyer flask, remove the erlenmeyer flask.
10. Rinse the top of the condenser and steam outlet into a waste beaker.
11. Continue distilling remaining samples, blanks and standards. When all samples, blanks and standards are distilled, the colorimetric determination can be performed.

C. Colorimetric Determination:

1. Transfer distilled blanks, standards and samples to 50 mL mixing cylinder and dilute to 50 mL with Milli-Q water. Mix.

2. Determine the TKN in the distillate colorimetrically as follows:

- Pour 25 mL of distillate or an aliquot diluted to 25 mL in a mixing cylinder.
- Add 1 mL of Nessler reagent. Stopper and mix by inverting several times.
- After 20 minutes, read the absorbances on the spectrophotometer set at 425 nm using the sipper cell. Zero the spectrophotometer to the distilled reagent blank.

Calculations:

1. Follow the calculations as stated in the ammonia nitrogen SOP. Make sure to calculate in any digestion dilution into the final result to obtain the TKN value.

Quality Control:

1. Establish a standard curve with the standards listed above plus a blank. Digest and distill the standard curve and blank. Record the absorbance check standard (1.00 mg/L) in the absorbance check book. The absorbances should remain consistent from run to run. If not, necessary troubleshooting must be performed before continuing (check wavelength, spectrometer bulb, solutions, etc.).
2. A digested/distilled calibration standard, (1.00 mg/L) blank, and known reference standard are to be analyzed at the beginning of the analytical run. The standard, must be within acceptable ranges and the blank less than the detection limit or troubleshooting must be performed.
3. A quality control calibration standard (1.00 mg/L) and a blank are to be analyzed, initially, and after every 10 samples. This standard needs to be carried through the digestion/distillation procedure. The last samples analyzed in the run are to be the calibration standard and blank. These standards must be within the acceptable ranges ($\pm 10\%$ of the true value) or the samples run after the last acceptable standard are to be reanalyzed.
4. Duplicate and spike a minimum of 1 out of 10 samples. If less than 10 samples are analyzed, a duplicate and spike are still required. Spike recoveries and duplicate results are to be within acceptable ranges.

SULFATE - AUTOANALYZER

Scope and Application: This method is applicable to drinking water, surface water, groundwater and wastewater.

Reference: EPA 1983, Method 375.2
Lachat Instruments 1986, Method 10-116-10-2-B

Detection Limit: 5.0 mg/L.

Optimum Concentration Range: 5.0 - 200 mg/L

Sample Handling: Refrigerate at 4°C and analyze within 28 days of collection.

Instrument Conditions:

1. Load time: 20 seconds
2. Inject period: 30 seconds
3. Inject to start of peak period: 9 seconds
4. Inject to end of peak period: 54 seconds
5. Cycle time: 50 seconds
6. Gain: 700
7. Zero: 200
8. Interference filter: 460 nm
9. Sample loop: 10 cm
10. Standards for curve set-up: 0, 25.0, 50.0, 100, 150, 200 mg/L.

Reagent Preparation: (Prepare fresh every 6 months, unless otherwise stated.)

1. Degassing with helium - 2 options:
 - a. Boil Milli-Q water vigorously for 5 minutes. Cool and store in cubitainer.
 - b. Bubble helium, using the fritted gas dispersion tube, through the Milli-Q water (15 min/20 L.) Store in cubitainer.
2. Carrier (0.3 ppm SO₄): In a 1 liter volumetric flask, add 0.3 mL of 1000 ppm stock sulfate solution and dilute to mark with degassed Milli-Q water.
3. Barium chloride solution (6.24M): In a 1 liter volumetric flask, dissolve 1.526 g of barium chloride dihydrate (BaCl₂·2H₂O) in 500 mL of Milli-Q water and dilute to 1 liter.
4. Hydrochloric acid (1.0N): In a 100 mL volumetric flask, containing approximately 80 mL of Milli-Q water, add 8.3 mL of concentrated hydrochloric acid and dilute to the mark with Milli-Q water.

5. Barium - MTB color reagent: (The purity of the methylthymol blue and the alcohol can be critical. USE THE SOURCES STATED BELOW).

In a dry 1000 mL volumetric flask, place 0.2364 g of methylthymol blue (3', 3" bis-N, N-bis carboxymethyl)-amino methylthymolsulfon-ephthalein pentasodium salt (Kodak No. 8068). Add 50 mL of barium chloride solution ("3" above). The solution may be used to aid in the transfer of the dye. Swirl to dissolve. Add 8.0 mL of the 1.0N HCL solution ("4" above) and mix - solution may turn orange. Add 142 mL deionized water and dilute to 1000 mL with ethanol (Aldrich 24.511.9) Mix. The pH of this solution should be 2.5. Prepare this solution the day before use and store it refrigerated in an amber bottle. NOTE: amount of methylthymol blue may be adjusted up/down for variance in lots of MTB.

6. Sodium hydroxide (50% stock solution): Cautiously dissolve 500 g of sodium hydroxide (NaOH) in 600 mL of Milli-Q water. Cool and dilute to 1 liter. Store in plastic bottle. CAUTION: The solution will become very hot!
7. Sodium hydroxide (0.18 N): In a 1 liter volumetric flask, add 14.4 mL of 50% sodium hydroxide ("6" above) to degassed Milli-Q water, and dilute to the mark.
8. Buffered EDTA (for cleaning manifold): In a 1 liter volumetric flask, dissolve 6.75 g ammonium chloride (NH₄Cl) in 500 mL DI water. Add 57 mL concentrated ammonium hydroxide and 40.0 g tetrasodium EDTA dihydrate. Dissolve by swirling; dilute to the mark with DI water.
9. Sulfate stock (1000 mg/L): Dry approximately 2 g of sodium sulfate (Na₂SO₄) at 105°C for 2 hours. Cool in a desiccator. In a 1 liter volumetric flask, dissolve 1.479 g of the dried sodium sulfate in Milli-Q water and dilute to 1 liter. (1.0 mL = 1.0 mg SO₄).
10. Working standard: (Prepare fresh every 2 months). Refrigerate.

<u>Concentration of Standard</u>	<u>Letter Identifier</u>	<u>Volume of Sulfate Standard</u>	<u>Dilute to</u>
0 mg/L	A	0	200 mL
25.0 mg/L	B	5.0	200 mL
50.0 mg/L	C	10.0	200 mL
100 mg/L	D	50.0	500 mL
150 mg/L	E	75.0	500 mL
200 mg/L	F	40.0	200 mL

NOTE: Final volumes are not the same!
Computer refers to standards by letter.

Preparation of Ion Exchange Column:

1. Make a slurry of approximately 0.5 g of BioRex 70, 50-100 mesh ion exchange resin in Milli-Q water.
2. Remove one column end from the glass column. Fill the column with water, then aspirate the slurry or allow it to settle by gravity to pack the column. Take care to avoid trapping air bubbles in the column and its fittings at this point and all subsequent operations.
3. After the resin has settled, replace the end fitting. To ensure a good seal, remove any resin particles from the threads of the glass, the column end and the end fittings. To store the column, the ends of the Teflon tubing may be joined with a union.
4. To test the effectiveness of the column, make up a standard of pure sodium sulfate and compare its peak height to an identical standard with hardness typical of the samples added. If the column is being depleted, the standard with hardness will read lower because the divalent cations are complexing the free MTB. The concentration of the standard should be mid-range. If depletion has occurred, repack the column with fresh resin.
5. Regenerating Resin: Batch regeneration is recommended because the hydrogen form of BioRex 70 can swell considerable more than the sodium form. collect the used resin in a small beaker or flask. Wash with dilute HCL until the wash tests free of calcium and/or magnesium. This procedure removes the divalent cations by converting the carboxylate exchange group to the protonated form - COOH. Convert the resin back to the sodium form by neutralizing with washes of 0.5M NaOH until the wash has a pH of 9 or greater. Rinse with deionized water for storage or repacking. A column may be used for 3-4 trays (approximately 150 samples) before it needs to be replaced.

Notes:

1. Samples must be diluted to obtain concentrations within the optimum working range.
2. Sulfate standards may be combined with alkalinity and chloride standards for use with the 3-channel method.
3. The gain and zero settings are guidelines and must be adjusted each day to optimize.
4. All coils (including waste coil) must be changed at least once each quarter to prevent build-up in lines.

4. Interferences:

- The cation exchange column removes multivalent cations. Run a mid-range sulfate standard containing a typical concentration of CaCO_3 periodically to check performance. Any decrease in peak height should indicate the need to regenerate or replace the resin. (At 600 ppm CaCO_3 , the column is good for 80 + injections.)
- Samples with pH <2 should be neutralized. High acid concentrations can displace multivalent cations from the column.
- Color will interfere. Dilute the sample and also spike the dilution to confirm the quality of the result.
- Turbidity - turbid samples may be filtered (use Whatman #1 or #4) prior to analysis on Lachat.
- Orthophosphate also forms a precipitate with barium at high pH. Check the response of pure orthophosphate standards, if samples are known to be high in PO_4^{3-} .

5. Troubleshooting:

A. Baseline noise with reagents pumping.

1. Noise with column in line but good baseline without column.
 - a. Repack column, air bubbles may be causing pulsing.
 - b. Check flow fit connectors and end fittings on column for blockage or leaks.
2. Noise with and without column in line.
 - a. Degas carrier and/or reagents. Fine bubbles cause sharp spikes on baseline.
 - b. Place a longer piece of manifold tubing on the outlet of the flow cell leading to the waste container. This method requires the use of the screw type flow cell.
 - c. Replace the pump tubes. The silicone tube, used for the color reagent, wears faster than the PVC pump tubes.
 - d. With water pumping in the lines, check all hydraulic connections for blockages, leaks, etc.

B. Baseline drift.

1. Clean the manifold with the buffered EDTA.
2. Turn the gain high and use the shortest sample loop possible. This improves the linearity of the calibration curve, prolongs the useful life of the column, and minimizes the build up of BaSO_4 on the manifold tubing.

System Operation:

1. Refer to "Auto Analyzer Operation start-up procedure." (SOP# LAA-Section A).
2. Pump reagents through the lines before inserting the column. Use a short piece of manifold tubing in place of the column. When all air has passed and the baseline is steady, turn off the pump and insert the column. The column should be placed in a vertical position with flow in the top and out the bottom. In this configuration, the column will operate effectively even if the resin packs down more to leave a gap at the top. Resume pumping.
3. Analyze an initial check standard, a blank, and a known reference at the beginning of each run. The blank must be less than the detection limit and the standards within acceptable limits.
4. To spike: Mix equal volumes of sample and 150 mg/L SO_4 standard (D) for a final spike level of 75 mg/L.
5. The calibration check standard is 100 mg/L (D).
6. To shut down, turn off pump and remove the column.

To remove the column:

- a. Turn off the pump.
- b. Remove the column.
- c. Join ends of the column with a union.
- d. Replace the column on the manifold with the short teflon tubing piece.
- e. Rinse manifold with Milli-Q water.
- f. Rinse manifold with EDTA cleaning solution.
- g. Continue with "Auto Analyzer Shut-down procedures" (SOP # LAA-Section B).

Quality Control:

1. Establish a standard curve with the standards listed above. Note that the calibration curve is calculated in a "piece-wise" fashion and is not linear. Be sure that calibration points describe smooth curve. If not, necessary troubleshooting must be performed before continuing (check reagents, pump tubing, valves, etc.).
2. A quality control calibration standard of 100 mg/L and a blank are to be analyzed, at a minimum, after every 10 samples. If less than 10 samples are analyzed, a calibration standard and blank are still required. The last samples analyzed in the run are to be the calibration standard and blank. These standards must be within the acceptable ranges or the samples run after the last acceptable check standard are to be reanalyzed.
3. Duplicate and spike a minimum of 1 out of 10 samples. If less than 10 samples are analyzed, a duplicate and spike are still required. Spike recoveries and duplicates are to be within acceptable ranges or data must be flagged appropriately.

Calculation:

1. Calculate with Lachat QuikChem software, in the concentration mode, using the IBM XT computer. See LAAC SOP for further detail.

NITRATE - AUTOANALYZER

Scope and Application: This method is applicable to drinking water, surface water, groundwater and wastewater.

Reference: EPA 1983, Method 353.2
Lachat Instruments, 1986

Detection Limit: 0.02 mg/L

Optimum Range: 0.02 - 2.00 mg/L $\text{NO}_3 + \text{NO}_2 - \text{N}$

Sample Handling: Preserve with sulfuric acid to pH <2 and refrigerate at 4°C. Analyze within 14 days. Alternatively, unpreserved samples, kept at 4°C can be analyzed within 48 hours of sampling.

Instrument Conditions:

1. Pump speed: 35
2. Cycle period: 50 seconds
3. Load period: 20 seconds
4. Inject period: 20 seconds
5. Inject to start of peak period: 22 seconds
6. Inject to end of peak period: 68 seconds
7. Gain: 450
8. Zero: 400
9. Interface filter: 520 nm
10. Sample loop: 17 cm
11. Standards for curve set-up: 0, 0.20, 0.50, 1.00, 2.00 mg/L
12. Column: (see reagents 7-10)

Reagent Preparation: (Prepare fresh every 6 months, unless otherwise stated.)

1. Degassed Milli-Q water (2 options):
 - a. Boil Milli-Q water vigorously for 5 minutes. Cool and store in a cubitainer, or
 - b. Bubble helium, using the fritted gas dispersion tube, through the Milli-Q water. Store in cubitainer. (15 min/20 L)
2. Stock nitrate standard (100 mg/L NO_3): In a 1 liter volumetric flask, dissolve 0.7218 potassium nitrate (KNO_3) in about 600 mL of Milli-Q water. Add 2 mL of concentrated H_2SO_4 as a preservative. Dilute to the mark. Store in a dark glass bottle.
3. Working stock nitrate standard (10 mg/L NO_3): Add 50 mLs D.I. water to a 100 mL volumetric flask. Add 0.2 mLs concentrated H_2SO_4 and pipet 10.0 mL of the stock nitrate standard. Dilute to the mark with DI water. Prepare fresh every 2 weeks.

4. Standards: (Prepare fresh every 2 weeks.) Preserve with 0.2 mL H_2SO_4 . Dilute to volume with D.I. water. Refrigerate.

<u>Concentration of Standard</u>	<u>Letter Identifier</u>	<u>Volume of NO_3 Standard</u>	<u>Dilute to</u>
0 mg/L	A	0	100 mLs
0.20 mg/L	B	2.0	100 mLs
0.50 mg/L	C	5.0	100 mLs
1.00 mg/L	D	10.0	100 mLs
2.00 mg/L	E	20.0	100 mLs

Note: Computer refers to standards by letter.

5. Sodium hydroxide (15M): To 250 mL of D.I. water, add 150.0g NaOH. SLOWLY! This solution will get very HOT! Swirl to dissolve. Store in a plastic bottle.

6. Ammonium chloride buffer solution: In a 1 liter volumetric flask, dissolve 85.0g of ammonium chloride (NH_4Cl)* and 1.0g of disodium ethylenediamine tetracetate dihydrate (EDTA) in approximately 800 mL D.I. water. Adjust the pH to 8.5 with 15M NaOH. Dilute to the mark and filter through a .45 μm filter. Refrigerate.

* See NOTES #5.

7. Sulfanilamide color reagent: In a 1 liter volumetric flask, add approximately 800 mL of Milli-Q water. Then add 100 mL concentrated phosphoric acid (H_3PO_4). Add 40.0g sulfanilamide and dissolve completely. Dissolve 1.0g N-1-naphthylethylenediamine dihydrochloride (NED) and dilute to one liter. Store in dark bottle at 4°C. Stable for 2 months when refrigerated.

8. Column Preparation:

- a. Cadmium preparation: Place 10-20g of coarse cadmium powder (granules) in a 250 mL beaker and wash with 50 mL of acetone, then distilled water, then two 50 mL portions of 1 M hydrochloric acid (8 mL concentrated hydrochloric acid plus 92 mL deionized water). Then rinse thoroughly with deionized water. If using cadmium for second time, rinse with 1 M hydrochloric acid before beginning process. CAUTION: Collect and store all waste cadmium. Wear gloves!
- b. Copperization: Prepare a 2% copper sulfate solution (20g $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ per liter of deionized water) and add a 100 mL portion to the cadmium prepared in "a" above. Swirl gently for about 5 minutes, then decant the liquid and repeat with a fresh 100 mL portion of 2% copper sulfate. Continue this process until colloidal copper is visible in the supernatant (a red-brown precipitate) and solution remains blue in color. Rinse with D.I. water until all colloidal copper is removed from the supernatant. Wash once with ammonium chloride buffer. The cadmium should be black or dark gray. The cadmium granules may be stored in a stoppered bottle in ammonium chloride buffer.

- c. Packing the column (wear gloves!): Place a small piece of polyurethane foam (or glass wool) loosely in the end of the glass tube. Insert the plugged end of the glass tube into the column end fitting. Cut a length of 0.032" id teflon tubing 3 to 4 inches longer than the column.

Insert the teflon tube in the end fitting and fill the whole tube with water, holding the flexible tube in a U-shape so that the ends are level. Place the second end fitting on the other end of the teflon tubing. (Placing a small funnel onto the end fitting may aid filling.) Taking care that no air bubbles are introduced, place the copperized cadmium granules in the column. Tap the column gently, every 1-2 cm, to pack the granules. When the column is packed to within about 5 mm of the end of the glass column, insert another foam plug, then the column end fitting. Store the column with the ends connected with a length of teflon tubing, as air pockets or having the column dry out will necessitate repacking. If air remains in the column, connect the column to the manifold and turn the pump on maximum. Tap column firmly until all air is removed.

- d. Column activation: The column must be activated before use or it will not reduce nitrate. This may be accomplished by pumping the 10 mg/L nitrate standard through the sample line. When the solution is injected, a brilliant pink color will be visible in the coil. The cadmium column efficiency should be above 80%, if less, the column must be repacked.

Notes:

1. Interferences:

- Build up of suspended matter in the reduction column will restrict sample flow. Since nitrate-nitrogen is found in a soluble state, the sample must be pre-filtered.
- Low results might be obtained for samples that contain high concentrations of iron, copper or other metals. EDTA is added to the samples to eliminate these interferences.
- Samples that contain large concentrations of oil and grease will coat the surface of the column. This interference is eliminated by pre-extracting the sample with an organic solvent.

2. Samples must be diluted to obtain concentrations within the optimum working range.
3. The gain and zero settings are guidelines and must be adjusted each day to optimize.
4. Color will interfere: dilute the sample and also spike the dilution to confirm the quality of the result. Record on data sheet.

5. ACS grade ammonium chloride has been found occasionally to contain significant nitrate contamination, so an alternative preparation for the ammonium chloride buffer (Reagent #6) is as follows:

In the hood, add 126 mL concentrated HCl to a 1 liter volumetric flask containing 500 mL degassed Milli-Q water. Mix. Add 95 mL ammonium hydroxide and 1.0 gm disodium EDTA. Dissolve and dilute to the mark. The pH should be $8.5 \pm .1$, adjust pH if necessary.

System Operation:

1. Refer to Auto Analyzer Operation - Start-up Procedure (IOP# LAA-section A).
2. After pumping reagents through the lines, turn off the pump and insert column, making sure that air bubbles are not introduced into the column.
3. Activate column if necessary. (See #8d. above.)
4. Analyze an initial calibration check standard, a blank, and a reference standard at the beginning of each run. The blank must be below the IDL and standards must be within the control limits.
5. To spike samples, mix equal volumes of sample and 1.00 mg/L standard for a final spike level of 0.50 mg/L.
6. The calibration check standard is 1.00 mg/L NO_3 (D).
7. If only nitrate is requested, nitrites must be analyzed and subtracted from the nitrate + nitrite value.
8. After use, turn off the pump and remove the column from the manifold.
9. Refer to Auto-Analyzer Shut-down Procedure. (IOP# LAA-Section B.)

Quality Control:

1. Establish a standard curve with the standards listed above. The derived concentrations for each calibration standard must be within 10% of the true value.
2. A quality control calibration standard of 1.00 mg/L and a blank are to be analyzed, at a minimum, after every 10 samples. If less than 10 samples are analyzed, a calibration standard and blank are still required. The last samples analyzed in the run are to be the calibration standard and blank. These standards must be within the acceptable ranges or the samples run after the last acceptable check standard are to be reanalyzed.
3. Duplicate and spike a minimum of 1 out of 10 samples. If less than 10 samples are analyzed, a duplicate and spike are still required. Spike recoveries and duplicates are to be within acceptable ranges or data must be flagged appropriately.

Calculation:

1. Calculate with Lachat Quikchem software, in the concentration mode, using the IBM XT computer.

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